Chapter 3B: Mercury and Sulfur Monitoring, Research and Environmental Assessment in South Florida

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SUMMARY

Elevated concentrations of mercury and sulfur are evident in the Everglades. The highly bioaccumulative form of mercury, methylmercury (MeHg), is a concern due to the neurotoxic threat it poses for Everglades wildlife and humans who consume Everglades fish. Sulfur is a concern because (1) as sulfate, it promotes methylation of mercury; (2) as sulfate or sulfide it affects the biogeochemical cycling of numerous elements including phosphorus; and (3) as sulfide, it may be toxic to aquatic plants and animals.

The very high mercury concentrations evident in fish in the Water Conservation Areas (WCAs) from the late 1980s to the early 1990s have declined substantially. Mercury levels in largemouth bass (LMB) (*Micropterus salmoides*) in the WCAs, however, remain generally above the proposed U.S. Environmental Protection Agency (USEPA) human health criterion for fish consumption for MeHg of 0.3 micrograms per gram (µg/g).

In contrast to the mercury reductions in LMB in the WCAs, mercury levels in these fish have increased or remain unchanged at high levels in Everglades National Park (ENP or Park). Concentrations within the Holey Land Wildlife Management Area (Holey Land WMA) show a downward trend in starting in 2008, which is opposite of the monotonic increase observed in previous years. In the ENP and WCAs, LMB and sunfish (*Lepomis* spp.) mercury levels are both above USEPA wildlife and human consumption criteria.

Across all water bodies within the Kissimmee Basin average LMB mercury levels range from 0.4 to 1.3 milligrams per kilogram (mg/kg), which is comparable to current levels found in the Everglades Protection Area (EPA) and the ENP. The similarity between largemouth bass levels in

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both regions suggests efficient mercury methylation and bioaccumulation is occurring within the Kissimmee Basin. Mercury levels within the basin also show a similar decreasing trend since 1990, which is cited to largely result from local source reductions.

Regarding sulfur, approximately 60 percent of the Everglades marsh area has sulfate concentrations greater than the Comprehensive Everglades Restoration Plan goal of 1 milligram per liter (mg/L) in surface water. It is probable that broad areas of the Everglades exhibit sulfate concentrations such that increased sulfate levels would enhance, and decreased sulfate concentrations reduce, MeHg bioaccumulation.

It is largely accepted that the mercury issue in South Florida wetlands is closely linked to sulfur-induced MeHg production, and it may not be possible to greatly reduce atmospheric mercury deposition to the Everglades. Accordingly, two practical approaches for addressing the Everglades MeHg problem are to review options for restoring the Everglades hydropattern that would minimize sulfur impacts to areas sensitive to MeHg production, and to evaluate the sources and sinks of sulfur in the Everglades Agricultural Area (EAA) and upstream areas with the goal of determining whether Best Management Practices for reducing sulfur loading to the Everglades would be feasible and effective for reducing sulfur impacts on the ecosystem. Some important future research should include (1) estimating agricultural-based sulfur applications to EAA soil for recent and past applications, (2) determining sulfur sources to Lake Okeechobee, (3) obtaining up-to-date EAA soil oxidation rates over a high resolution scale, and (4) estimating groundwater sulfur inputs to EAA canals.

The Florida Department of Environmental Protection (FDEP) and the South Florida Water Management District (SFWMD or District) continue to promote improved understanding of the sources, transformations, and toxicity of mercury in the Everglades, in support of natural resource management decisions through ongoing research. This chapter serves to update previously reported findings in earlier consolidated reports, with supporting data on mercury provided in Appendices 3B-1, 3B-2, and 5-6. This chapter, together with its appendices and Appendix 5-6, meet the Everglades Forever Act (EFA) requirement that the District and the FDEP shall annually issue a peer-reviewed report that summarizes all data and findings of mercury research and monitoring in South Florida. Additional detailed scientific information can be found in mercury chapters of the 1999 Everglades Interim Report, 2000–2004 Everglades Consolidated Reports, and 2005–2009 South Florida Environmental Reports.

NEW FINDINGS

New findings and issues of continuing concern summarized below are drawn from this chapter and from related appendices. For additional information on mercury monitoring and assessment for fish [largemouth bass, sunfish, mosquitofish (*Gambusia holbrooki*)], juvenile great egrets (*Casmerodius albus*), surface water, and atmospheric deposition for the EPA and the Stormwater Treatment Areas, see Appendices 3B-1 and 5-6.

- Since 1988, 3,033 LMB have been collected from WCAs 1, 2, and 3 for mercury determinations. System-wide median mercury concentrations varied between 1.75 µg/g in 1988 (range, 1.20–3.4 µg/g; n = 12) and 0.30 µg/g in 2007 (range, 0.04–2.0 µg/g; n = 263). The 2008 median changed little from the previous year (median = 0.38 µg/g; range, 0.02–1.5 µg/g; n = 241). Most importantly, median concentrations declined 62 percent between 1988 and 2008 and have remained below 0.5 µg/g since 1998. Nonetheless, median concentrations in LMB continue to exceed the USEPA human-health fish tissue MeHg criterion of 0.3 µg/g (USEPA, 2001) and, since 1998, over 50 percent of all LMB (n = 1,511) exceed the USEPA criterion.

- Further to the south in Shark River Slough (in the ENP), a total of 490 LMB have been collected for mercury analyses from two sites each year (L67F1 and ENPNP) since 1989. Results show high mercury concentrations in these fish. A decrease in the median concentration during 2008 to 0.78 µg/g was encouraging (range, 0.30–3.50 µg/g; n = 41); however, 2009 represented a return to a median well in excess of 1.0 µg/g. The 2009 median is represented only by site ENPNP because data from L67F1 was not available at the time this report was written.

- Mosquitofish collected from marsh sites within the WCAs and the ENP had total mercury levels ranging from 0.007 µg/g at site WCA2F1 (WCA-2, F1) to 0.16 µg/g at site WCA35ALT. The average basinwide concentration for 2008 was 0.06 µg/g. This average concentration level represents a 20 percent decrease from the basinwide mean concentration in 2007. The grandmean for the period of record (POR) (1998–2008) over all basins is 0.075 µg/g. Overall, based on arithmetic means, mosquitofish show a significant decrease in total mercury (THg) concentration in 2008. (See Appendix 3B-1 for more detail.)

- Sunfish collected from marsh sites within the WCAs and the ENP had total mercury levels ranging from 0.01 µg/g at site WCA2F1 to 0.65 nanograms per gram (ng/g) at site WCA35ALT. The basinwide average concentration in sunfish for 2008 was 0.21 ng/g, representing a 10 percent increase from 2007. When the dataset was censored to only consider bluegill sunfish (*L. macrochirus*) and length-standardized mercury levels, sites CA35ALT, WCA2U3, and CA33ALT had statistically higher THg levels than all other sites. Stations HOLYBC, WCA2U3, WCA33, and LOX4 show statistically significant temporal increases since the POR (1998–2008) began. The grandmean for the POR over all basins is 0.17 ng/g. Based on arithmetic means, sunfish showed an overall slight increase in THg concentration in 2008. (See Appendix 3B-1 for more detail.)

- North of the ENP in the remaining waters of Florida, mercury continues to be a significant water quality problem. It has been suggested that at least 1,300 lakes, not including streams and coastal areas, are impaired due to mercury bioaccumulation in fish. From 1983–2008, annual median mercury concentrations in LMB from areas in the Northern Everglades and farther north in Florida varied between a high of 0.73 µg/g (range, 0.08–1.18 µg/g; n = 114) in 1988 and a low of 0.23 µg/g (range, 0.01–2.3; n = 601) in 2008.

- Median concentrations for Shark River Slough in the ENP, the WCAs, and areas north of the ENP for the sampling periods from July 2008–June 2009 were 0.78, 0.38, and 0.23 µg/g, respectively, and were significantly different (Kruskal-Wallis, p < 0.0001; df = 2; H = 66) from each other. In spite of a great deal of overlap in mercury concentration in fish, the median for north of the ENP was significantly lower (p < 0.005) than the median for the WCAs (Mann-Whitney Test). Fish mercury concentrations in water bodies north of the Everglades vary greatly but tend to be lower than those from the EPA.

MERCURY IN EVERGLADES FISH AND WILDLIFE

HISTORICAL MONITORING OF MERCURY IN BIOTA

Elevated levels of mercury in biota from Everglades National Park (ENP or Park) were first reported in Ogden (1974). In 1988, reports of mercury levels in largemouth bass (LMB) (*Micropterus salmoides*) in the Water Conservation Areas (WCAs) exceeding 1 milligram per liter (mg/L) [1 L fish tissue homogenate ≈ 1 kilogram (kg)] prompted more widespread sampling of both fish and wildlife. As a result of further sampling, Ware et al. (1990) reported elevated mercury levels in alligators (*Alligator mississippiensis*), crayfish (*Procambarus fallax*), softshell turtles (*Apalone ferox*), pig frogs (*Rana grylio*), mottled ducks (*Anas fulvigula*), white-tailed deer (*Odocoileus virginianus*), and the endangered Florida panther (*Felis concolor*). Since that time, mercury has been a chronic water quality problem in the Everglades Protection Area (EPA), impacting humans and fish-eating wildlife because of excessive bioaccumulation of mercury in fish. High concentrations of mercury in fish have not only been documented in the freshwater reaches of the EPA (Loftus et al., 1998; Axelrad et al., 2009), but also downstream in Florida Bay (Strom and Graves, 2001; Evans et al., 2003) and the Gulf of Mexico (Adams et al., 2003; Axelrad et al., 2009). In response to concentrations of mercury in sport fish exceeding human health criteria, fish consumption advisories have been issued for Florida Bay, the Gulf of Mexico, and fresh waters within the ENP, WCAs, and other surrounding areas (FDOH, 2008a). In addition, one wildlife species, the pig frog, has a limited-consumption advisory (FDOH, 2008b).

Fish and wildlife monitoring is important to assess human and wildlife risks from consumption of mercury-contaminated fish, and is also useful to assess spatial and temporal trends in mercury bioaccumulation. This chapter reports on fish sampling activities within the Greater Everglades during the past 20 years. Monitoring objectives include documenting trends in fish mercury and assessing human health and ecological risk from consumption of fish.

MERCURY IN FISH — CURRENT-YEAR SAMPLING

Fish Collection, Analysis and Mercury Concentration Normalization

Largemouth bass (and other sport fish not discussed in this report) were collected for this report during the current-year sampling periods from July 2008 through June 2009 from the EPA and other South Florida sites using direct-current electrofishing equipment. In the laboratory, LMB were weighed, measured, sexed, and the sagittal otoliths were removed for determination of age as described by Taubert and Tranquilli (1982). An entire skinless axial muscle fillet was homogenized and an aliquot submitted to the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee where total mercury (THg) determinations were made using U.S. Environmental Protection Agency (USEPA) Method 245.6 (Mercury in Tissues by Cold Vapor AAS). The detection limit (MDL) for this method was 0.02 mg/L. All results are reported on a wet-weight basis as micrograms per gram [(µg/g), which is the same as parts per million (ppm) or milligrams per kilogram (mg/kg)]. More than 85 percent of the mercury found in top-level predatory fish such as LMB is in the form of methylmercury (MeHg) (Grieb et al., 1990; Bloom, 1992); therefore, analyses were conducted for total mercury (THg) with the assumption made that THg represents the MeHg concentration in the samples.

Results of mercury monitoring in LMB provides a measure of MeHg exposure integrated both spatially and temporally. This is particularly relevant across the Everglades landscape where fish can move over vast areas in response to changes in hydroperiod. Presumably, integration of mercury occurs under varying ambient mercury concentrations in prey. Mercury exposures in LMB are also reflective of variations in fish size and age, population turnover, trophic position,

and trophic exchange rates. A distinct advantage to using LMB as a monitoring tool is their ability to accumulate high concentrations of mercury, thus allowing differentiation of concentration gradients among hydrologic compartments within the EPA. LMB are also readily available, have well understood feeding ecology and life histories, and are directly relevant to public health policy.

In this report, data are presented by two distinct methods in order to compare and contrast both regional and site-specific trends in fish mercury concentrations within the EPA. Moreover, comparisons with trends observed at sites in the Northern Everglades and North Florida are made to provide contrast with trends observed within the EPA. First, regional trends within the EPA are discussed utilizing the median concentrations in LMB collected from multiple sites within each of three distinct regions including the ENP, the WCAs, and lakes and rivers north of and including Lake Okeechobee. Second, site-specific trends in normalized mercury concentrations in LMB are presented for 10 sites located in the Southern Everglades (including sites within the EPA), two sites in the Northern Everglades, and one site in North Florida. Finally, a more detailed discussion on trends in average LMB mercury levels in the Kissimmee Chain of Lakes (KCOL) within the Northern Everglades is presented.

Although not presented here, waterbody-specific risk assessments are conducted on all sampled public water bodies. The Florida Department of Health (FDOH) conducts health assessments and publishes waterbody-specific fish consumption advisories for LMB and other freshwater sport fish including sunfish (*Lepomis* spp.), black crappie (*Pomoxis nigromaculatus*), catfish (*Pterygoplichthys multiradiatus*), and several exotic species within the EPA and other state waters. Assessments are conducted based on priority rankings by fisheries managers, observed trends within a region or site, and the need determine if the waterbody is "impaired" due to mercury pollution and in need an updated Total Maximum Daily Load (TMDL) assessment. Published results of waterbody specific risk assessments can be found at http://www.doh.state.fl.us/environment/medicine/fishconsumptionadvisories/index.html.

Regional Trends in the Everglades Protection Area

Largemouth bass collected from sites within the EPA, including sites within the WCAs and the ENP (see **Figure 3B-1**), are summarized by region to investigate regional trends in mercury bioaccumulation in fish. Comparison is made against trends for LMB collected from the waters of Florida north of the EPA.

From July 2008–June 2009, 241 LMB were collected from the WCAs and 41 were collected from Shark River Slough in the ENP and summarized to assess regional trends in mercury concentrations. In order to compare and contrast LMB mercury trends in the WCAs and Shark River Slough with the remainder of Florida, this chapter draws on data collected from sites north of the EPA where, during the same time period, 601 LMB were collected from sites in rivers and lakes in the Northern Everglades and Central and North Florida.

Since 1988, 3,033 LMB have been collected from WCAs 1, 2, 3, at sites identified in **Figure 3B-1** and from other sites for mercury analyses. System-wide median mercury concentrations varied between 1.75 µg/g in 1988 (range; 1.20–3.4 µg/g; n = 12) and 0.30 µg/g in 2007 (range; 0.04–2.0 µg/g; n = 263) (**Figure 3B-2**). The 2008 median changed little from the previous year (median = 0.38 µg/g; range; 0.02–1.5 µg/g; n = 241). Most importantly, median concentrations declined 62 percent between 1988 and 2008 and have remained below 0.5 µg/g since 1998. Nonetheless, median concentrations in LMB continue to exceed the USEPA human-health fish tissue MeHg criterion of 0.3 µg/g (USEPA, 2001) and, since 1998, over 50 percent of all LMB (n = 1,511) exceeded the USEPA criterion. It is evident that high rates of mercury bioaccumulation continue to be a problem in the WCAs with fish consumption advisories covering nine species of fish across all waters within the WCAs.

Further to the south in Shark River Slough in the ENP, 490 LMB have been collected for mercury analyses from two sites each year, L67F1 and ENPNP, since 1989 (**Figure 3B-1**). Results show high mercury concentrations in fish. A decrease in the median concentration during 2008 to 0.78 µg/g was encouraging (range; 0.30–3.50 µg/g; n = 41); however, 2009 represented a return to a median well in excess of 1.0 µg/g (**Figure 3B-3**). The 2009 median is represented only by site ENPNP since data for L67F1 was not available at the time of this report.

LMB mercury concentrations in Shark River Slough continue to exceed the USEPA MeHg criterion with all LMB collected (except one) since 1998 exceeding 0.3 µg/g (range; 0.23–4.80 µg/g; n = 490). The Florida Department of Health continues to issue no-consumption advisories for LMB, common snook (*Centropomus undecimalis*), spotted sunfish (*L. punctatus*), and yellow bullhead (*Ameiurus natalis*) from Shark River Slough. They further recommend limited consumption of redear sunfish (*L. microlophus*), bluegill (*L. macrochirus*), and the exotic Mayan cichlid (*Cichlasoma urophthalmus*) from Shark River Slough waters (FDOH, 2008a). Mercury bioaccumulation in Shark River Slough appears to be elevated over other areas of the ENP (Axelrad, 2009), but the entire park has advisories urging limited consumption of fish. Of particular concern in the ENP are the impacts of mercury on estuarine species in downstream reaches of Shark River Slough where processes affecting bioaccumulation of mercury are not well understood.

In the remaining waters of Florida, mercury continues to be a significant water quality problem. It has been suggested that at least 1,300 lakes, not including streams and coastal areas, are impaired due to mercury bioaccumulation in fish (FDEP, 2007) and the FDOH currently advises limited fish consumption from over 300 water bodies, including lakes and streams, throughout the state. From 1983–2008, annual median mercury concentrations in LMB from the sites north of the EPA varied between a high of 0.73 µg/g (range; 0.08–1.18 µg/g; n = 114) in 1988 and a low of 0.23 µg/g (range; 0.01–2.3; n = 601) in 2008 (**Figure 3B-4**).

Mercury concentrations from the three regions reported above are shown for the 2008 sample year in **Figure 3B-5**. Median concentrations for Shark River Slough, the WCAs and north of the Everglades were 0.78, 0.38, and 0.23 µg/g, respectively and were significantly different (Kruskal-Wallis; p < 0.0001; df = 2; H = 66) from each other. In spite of a great deal of overlap in mercury concentration in fish, the median for the sites north of the EPA was significantly lower (p < 0.005) than the median for the WCAs (Mann-Whitney Test). Fish mercury concentrations in LMB from waters in the rest of the state (**Figure 3B-4**) tend to be lower than those from the EPA.
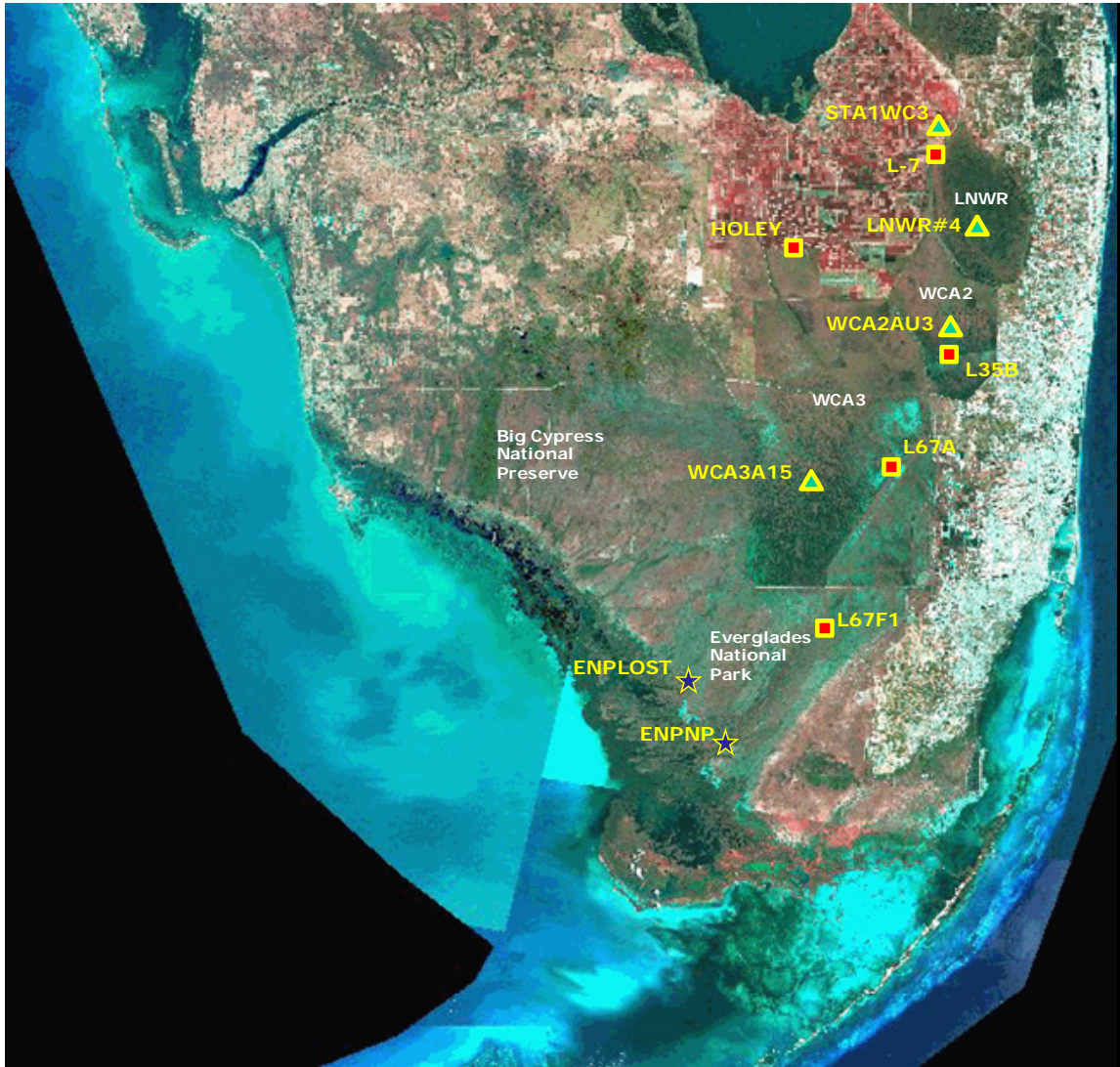
Figure 3B-1. Location of 10 long-term monitoring sites in the Everglades Protection Area, Stormwater Treatment Area 1 West, and Holey Land Wildlife Management Area. Site L67F1, located in the ENP, is not a long-term monitoring site, but is included because of its importance to annual regional trends assessments. Marsh sites are indicated by a green triangle, canals by a red square, and estuarine creeks by blue star.
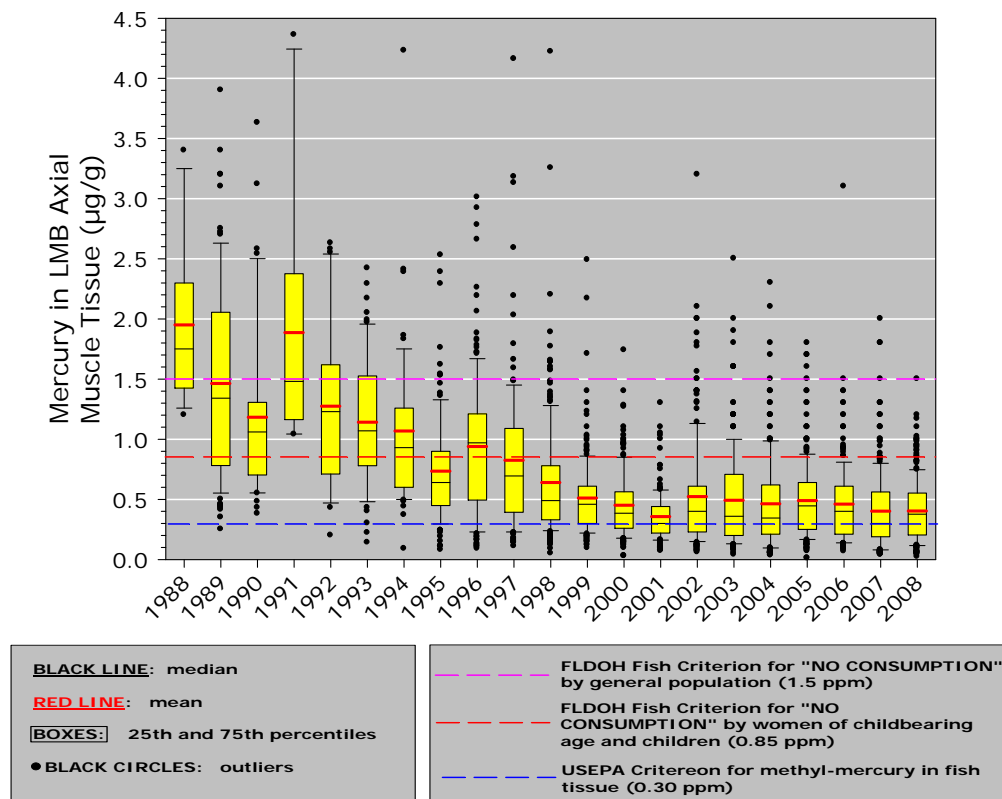
Figure 3B-2. Annual summaries of mercury concentrations in 3,033 largemouth bass (LMB) (*Micropterus salmoides*) collected from canal and marsh sites in Water Conservation Areas 1, 2, and 3 from 1988–2008.
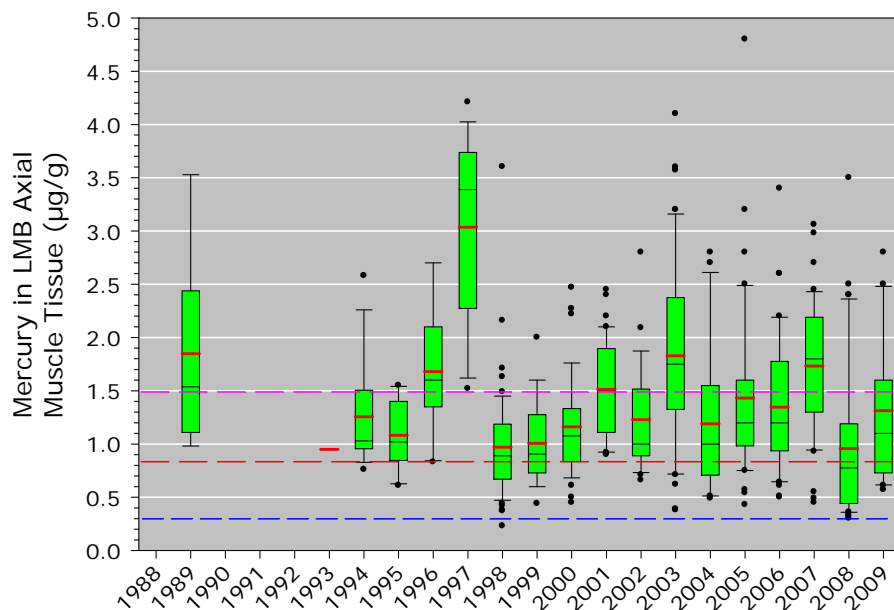

Figure 3B-3. Annual summaries of mercury concentrations in 490 largemouth bass collected from sites L67F1 and ENPNP in the Shark River Slough of Everglades National Park between 1989 and 2009. See **Figure 3B-2** for legend.
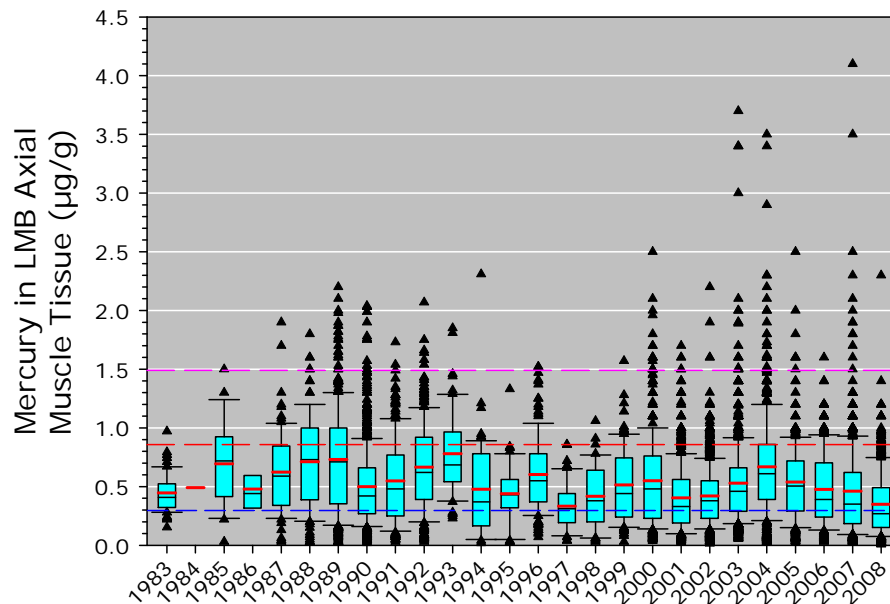
Figure 3B-4. Annual summaries of mercury concentrations in 8,163 largemouth bass collected from north of the EPA including lake and stream sites north of, and including, Lake Okeechobee through the panhandle from 1983–2008. The black central line represents the annual median and the red line the mean. Black boxes represent the 25th and 75th percentiles and the error bars represent the 10th and 90th percentiles. Black circles are outliers.
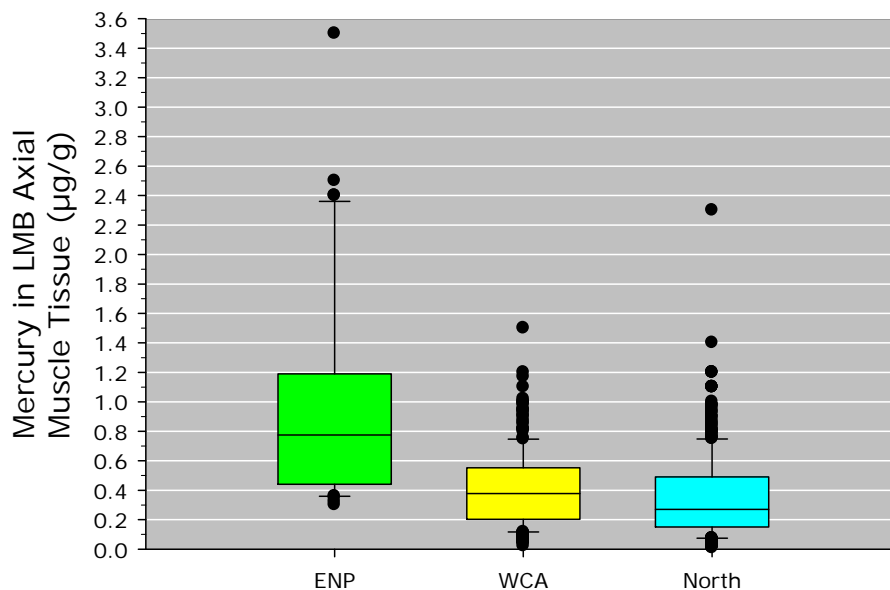

Figure 3B-5. Box plots showing mercury concentrations from Everglades National Park (n= 41), the WCAs (n = 241), and sites north of the EPA (n = 601) including lake and stream sites north of Lake Okeechobee through the panhandle showing the median mercury concentrations during 2008.

Site-Specific Trends

Localized trends in LMB mercury levels were monitored at 17 locations in Florida including 10 within the Southern Everglades that are described in this report along with two sites in the Northern Everglades and one site in North Florida. The 10 sample sites within the Southern Everglades are situated along a north-to-south transect extending from Stormwater Treatment Area 1 West (STA-1W) into the EPA. Within the EPA, sites were located in the Holey Land Water Management Area (WMA), WCA-1 (n = 2), WCA-2 (n = 2), WCA-3 (n = 2), and the ENP (n = 2). In the Northern Everglades, long-term monitoring in East Lake Tohopekaliga and Lake Tohopekaliga is reported, while monitoring in the Suwannee River 15 kilometers from its confluence with the Gulf of Mexico is reported for North Florida. Sites are sampled annually, but start dates and, therefore, periods of record for LMB collections varies among sample sites (**Table 3B-1**). Collections began in the Suwannee River in 1988, but in the EPA the longest POR for a site is at the L67A canal where sampling started in 1990.

At each site, 20 LMB ranging in length from 200–500 mm were collected each year and analyzed for THg in muscle tissue. LMB mercury concentrations were normalized by age to account for size-dependent bioaccumulation of mercury and also to correct for variations in sample size distributions, sex, and collection date. Standardization to fish size or age in order to normalize contaminant concentrations in fish is a common practice (Hakanson, 1980; Wren and MacCrimmon, 1986; Sorenson et al., 1990), and normalization to age has proven effective for spatial and temporal comparison of LMB mercury data for Florida (Lange et al., 1993 and 1994). Normalization of monitoring data is necessary to assess the relationships between mercury bioaccumulation and changes in mercury loading to the system, or other environmental factors (e.g. sulfate loading) which would affect mercury bioaccumulation (Wiener et al., 2006).

Therefore during this study, LMB mercury levels were standardized to an expected age-3 mercury concentration (EHg3) by linear regression of mercury concentration on age for each site and calculating the expected mercury concentration in a three-year old LMB for each sample event. Where no significant relationship between mercury and age was observed (p > 0.05), the mean mercury concentration was reported. These data are reported in a series of site-specific reports indicating spatial and temporal trends in LMB mercury concentrations. Emphasis has been given to temporal analyses of data but consideration was also given to spatial distributions of mercury bioaccumulation in the EPA as well. A total of 17 long-term monitoring sites were established in Florida; 13 are discussed in this report including 10 sites identified within the EPA in **Figure 3B-1**.

Location names, site descriptions, POR, and age-standardized mercury concentrations in LMB (EHg3) are given for select sites in **Tables 3B-1** and **3B-2**. Within the EPA, sampling sites were located along a transect starting in STA-1W and moving south through WCAs 1, 2, 3, and into the ENP. A site is also located north of WCA-3 in the Holey Land WMA (**Figure 3B-1**). Spatial and temporal trends for these long-term monitoring stations are reported in **Table 3B-2**. **Figures 3B-6** through **3B-12** show these trends for the WCAs, the ENP, Holey Land WMA, East Lake Tohopekaliga, and the Suwannee River. The POR and number of sampling events vary among sites due to differences in initial sampling dates and inability to collect LMB samples during some years; however, data generally report back to the mid-1990s or earlier. During October and November 2008, 138 LMB were collected from WCAs 1, 2, and 3; 20 from the ENP; 20 from STA-1W; and 20 from Holey Land WMA for use in analyses of spatial and temporal trends among sites. During March 2009, 40 LMB were collected from two more locations in the ENP. Many of these LMB were utilized in the regional assessments discussed previously.

Site-specific trends in EHg3 at sites located in WCAs 1, 2, and 3 (**Figures 3B-6**, **3B-7**, and **3B-8**, respectively) generally reached maximum values from 1992–1996 which ranged between 0.61 and 2.39 µg/g (**Table 3B-2**). These maximal values occurred near the beginning of the POR for each site and, based on similar trends within the WCAs as a whole (**Figure 3B-2**), it is logical to conclude that EHg3 values were likely higher in the late 1980s and early 1990s prior to initiation of monitoring at these sites. Minimal EHg3 values were observed much later at these sites, occurring from 1998–2008 with a range of 0.09 to 0.51 µg/g. These lower levels represent declines in EHg3 of 61 to 89 percent across the WCAs (**Table 3B-2**) at both canal and marsh sites. In WCA-3, the EHg3 reached its minimum in 2008 at sites L67A and WCA3A15 (**Table 3B-2**) and represent a nearly 90 percent decline in EHg3 during the entire POR. In contrast to this trend, EHg3 at site WCA2-U3 reached 1.01µg/g in 2008, while at the same time a moderate decline was observed at site L35B (also within WCA-2) from the previous year (**Figure 3B-7**). Sites co-located within a WCA typically follow similar trends; however, differences observed at sites within WCA-2 are not unexpected due to gradients in MeHg concentrations across WCA marshes (Gilmour et al., 1998; Cleckner et al., 1999; Scheidt and Kalla, 2007) and canals (Hurley et al., 1998). Overall, EHg3 declined between 21 and 84 percent during the entire POR at six sites found in WCAs 1, 2, and 3 (**Table 3B-2**).

The EHg3 at site STA1WC3, located within a man-made wetland, STA-1W, varied little and had a range of 0.05 to 0.12 µg/g from 1995–2008 (**Table 3B-2**). Within STA-1W, mercury levels in LMB are nearly an order of magnitude lower than those in the WCAs and the ENP (Gabriel et al., 2009) and represent some of the lowest mercury concentrations found in LMB in all of Florida.

Of concern within the EPA are levels of EHg3 in the ENP and in the Holey Land WMA. In the ENP, site ENPNP is located within the Shark River Slough drainage while site ENPLOST is located further north and within waters draining Big Cypress National Preserve (**Figure 3B-1**). Historically, EHg3 concentrations have been higher in Shark River Slough at site ENPNP; however from 2007–2009, EHg3 at both sites converged near 1 µg/g (**Figure 3B-9**). This represents a 76 percent increase in EHg3 at site ENPLOST for the POR and a 50 percent decline in EHg3 at site ENPNP during the POR (**Table 3B-2**). Both sites were initially sampled in 1994 but no LMB were collected from ENPLOST from 2001–2006. Site ENPNP, along with site L67F1 represent the regional trends for the Shark River Slough presented in **Figure 3B-1**. Although the standardized mercury concentration at site ENPNP in 2009 was 1.18 µg/g (**Table 3B-2**) and the median for the region was 1.10 µg/g (**Figure 3B-3**), individual LMB mercury concentration ranged from 0.57 to 2.8 µg/g (n = 20). Moreover, south of this area in Florida Bay, mercury levels remain elevated with many species having average mercury levels in muscle tissue around 1 µg/g (Evans et al., 2003; Strom and Graves, 2001). Indeed, levels of mercury in the ENP and in particular, Shark River Slough, continue to exceed the USEPA human-health fish tissue MeHg criterion of 0.3 µg/g (USEPA, 2001).

To the north of WCA-3 and outside the EPA is the Holey Land WMA where long-term sampling at site HOLEY (**Figure 3B-10**) has been of a shorter duration than sites in the EPA. Monitoring likely caught the tail end of declines that occurred concurrent with those in the WCAs in the late 1990s. EHg3 was minimal in 1999 at 0.27 µg/g but climbed quickly to 0.86 µg/g in 2006 (**Table 3B-2**). In 2008, EHg3 was 0.52 µg/g, an encouraging downward trend but still in excess of human health criteria.

Within the Kissimmee Chain of Lakes (KCOL), two long-term monitoring sites were established in 1989 in Lakes Tohopekaliga and East Tohopekaliga (**Table 3B-1**). From maximum EHg3 concentrations during the first year of sampling at both sites, concentrations of mercury have declined by 36 and 75 percent in Lakes Tohopekaliga and East Lake Tohopekaliga, respectively, during the entire POR (**Table 3B-2**). Most noteworthy are the consistent downward

trends in EHg3 in East Lake Tohopekaliga (**Figure 3B-11**) where declines have resulted in the lowest EHg3 for the entire POR of 0.28 µg/g in 2009. Further north in Florida, the long-term monitoring site on the Suwannee River is located approximately 15 river kilometers upstream of the mouth of the river at Fowlers Bluff. Twenty-two annual samples have been collected from this site from 1988–2009 (**Table 3B-1**) where the EHg3 has declined 49 percent over the course of the POR (**Table 3B-2**). However, trends at this site are inconsistent and a great deal of variation occurs in EHg3 between years (**Figure 3B-12**). This perhaps illustrates a quick response in LMB mercury bioaccumulation to fluctuations in ambient MeHg levels due to inundation of floodplain habitats within the river basin. From 2008–2009, mercury concentrations at a collection site in the Suwannee River are roughly half of what was observed in the WCAs and the ENP, thus revealing a rough statewide north-to-south concentration gradient (**Figure 3B-5**).

It has been hypothesized that reductions in mercury emissions from local sources during the early 1990s resulted in reductions in fish mercury concentrations in parts of Florida (Atkeson, 1999). Despite localized reductions in EHg3 concentrations, mercury concentrations have remained constant or increased in other locations both within and outside the EPA overall. Likely, rapid reductions in fish mercury will occur if and when sources are reduced (Harris et al., 2007); however, redistribution of existing legacy mercury could delay fish mercury reductions.

Table 3B-1. Location and description of reported sites for long-term monitoring of mercury bioaccumulation in largemouth. The period of record (POR) and number of annual samples collected over the POR are shown. Sampling events typically represent one collection each year but may vary. Site locations in the Southern Everglades can be found in **Figure 3B-1**.

Location/Site	Description	Site POR	Sample Events
Tohopekaliga	Northern Everglades, Kissimmee Basin	1989-2009	23
East Lake Tohopekaliga	Northern Everglades, Kissimmee Basin	1989-2009	23
Suwannee River*	North Florida	1988-2009	22
Stormwater Treatment Area 1W			
STA1WC3	Interior marsh, two sites in Cell 3	1995-2008	15
Holey Land WMA			
HOLEY	North Borrow Canal connected to marsh	1996-2008	13
Water Conservation Area 1			
LNWR#4	Marsh	1995-2008	14
L-7	L-7 conveyance canal	1995-2008	14
Water Conservation Area 2A			
WCA2AU3	Marsh	1993-2008	17
L35B	L-35B conveyance canal	1993-2008	17
Water Conservation Area 3A			
WCA3A15	Marsh	1993-2008	15
L67A	L-67A conveyance canal	1990-2008	22
Everglades National Park			
ENPLOST	Lostman's Creek, estuarine, Big Cypress National Preserve drainage	1994-2009	11
ENPNP	North Prong Creek, estuarine, Shark River Slough	1994-2009	17

* Not within the boundaries of the South Florida Water Management District;
data included for site-specific comparison only.

Table 3B-2. Trends in age-standardized mercury levels in largemouth bass (EHg3) for various periods of record (POR) at 10 long-term monitoring sites and for comparison, three sites in central and north Florida. The percent change for the entire period of record (POR) is shown along with historic minimum and maximum values and the percent change between them. The current EHg3 and the percent change from the minimal concentration to current are shown. Sites are aligned from north to south and EHg3 is reported as µg/g = mg/kg = ppm).

Location/Site	Site POR	POR %Change	Historic Levels			Current Levels	
			Max EHg3(Yr)	Min EHg3(Yr)	% Change Max to Min	EHg3(Yr)	% Change Min to Current
Lake Tohopekaliga	1989-2009	-36	0.77*(1989)	0.24 (2003)	-69	0.40 (2009)	67
East Lake Tohopekaliga	1989-2009	-75	1.12 (1989)	0.28 (2009)	-75	0.28 (2009)	NA
Suwannee River	1988-2009	-49	0.89 (1992)	0.18 (2003)	-80	0.28 (2009)	NA
Stormwater Treatment Area 1W							
STA1WC3	1995-2008	-23	0.12 (1996)	0.05 (2004)	-57	0.08 (2008)	60
Holey Land WMA							
HOLEY	1996-2008	1	0.86 (2006)	0.27 (1999)	-68	0.52 (2008)	93
Water Conservation Area 1							
LNWR#4	1995-2008	-62	0.88 (1996)	0.17*(2003)	-81	0.30 (2008)	76
L-7	1995-2008	-37	0.61 (1996)	0.09 (2004)	-85	0.25 (2008)	177
Water Conservation Area 2A							
WCA2A-U3	1993-2008	-21	1.27 (1993)	0.48 (2001)	-62	1.01 (2008)	110
L35B	1993-2008	-44	1.32 (1994)	0.51 (1998)	-61	0.57 (2008)	12
Water Conservation Area 3A							
WCA3A15	1993-2008	-84	2.39 (1993)	0.26*(2008)	-89	0.26*(2008)	NA
L67A	1990-2008	-79	1.83*(1992)	0.24*(2008)	-87	0.24*(2008)	NA
Everglades National Park							
ENPLOST	1994-2009	76	1.14 (1997)	0.62 (1996)	-46	0.87 (2009)	49
ENPNP	1994-2009	-50	2.36 (1994)	0.79 (1998)	-67	1.18 (2009)	13
10-Site Average		**-32**	**1.28**	**0.35**	**-70**	**0.51**	

*Mean THg reported for these sites due to insignificant ($p > 0.05$) relationship between fish mercury and age: LNWR#4 in 2003, L67A in 1992 and 2008, and WCA3A15 in 2008.
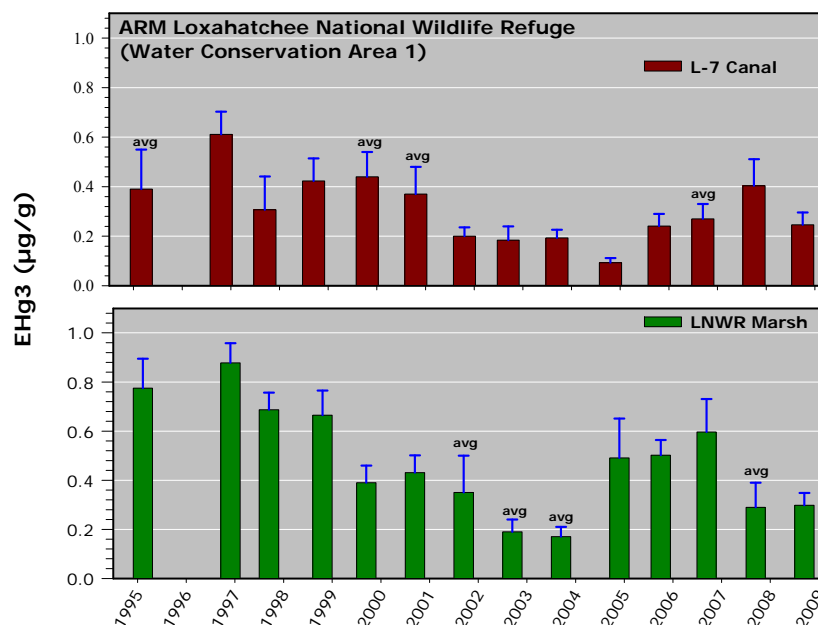
Figure 3B-6. Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval in LMB at long-term monitoring sites located within Water Conservation Area 1. The average THg concentration is reported where calculation of the EHg3 was not appropriate.
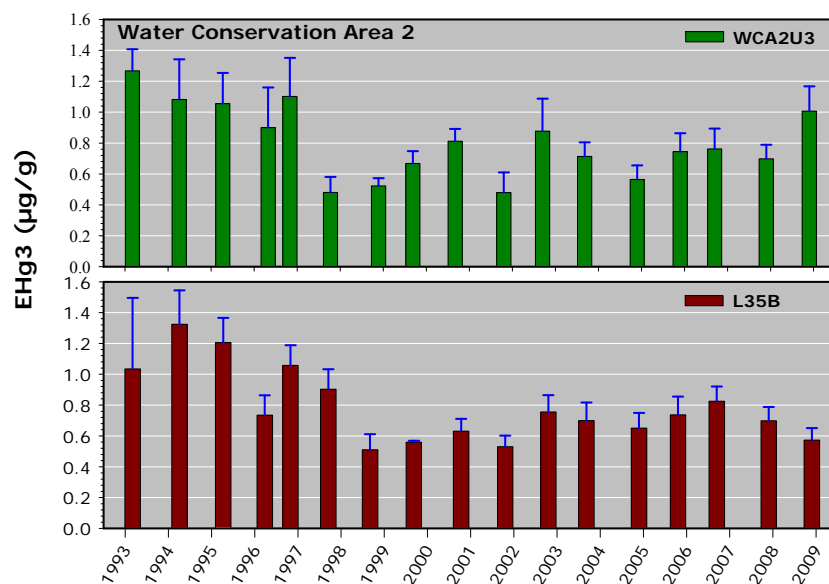

Figure 3B-7. Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval in LMB at long-term monitoring sites located within Water Conservation Area 2.

Figure 3B-8. Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval in LMB at long-term monitoring sites located within Water Conservation Area 3. The average THg concentration (avg) is reported where calculation of the EHg3 was not appropriate.
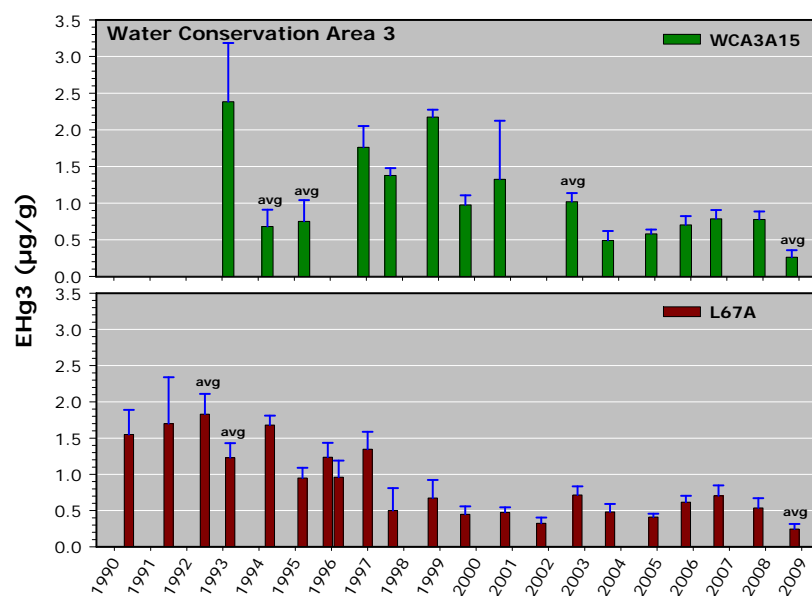

Figure 3B-9. Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval in LMB at long-term monitoring sites located within Everglades National Park. The average THg concentration is reported where calculation of the EHg3 was not appropriate.
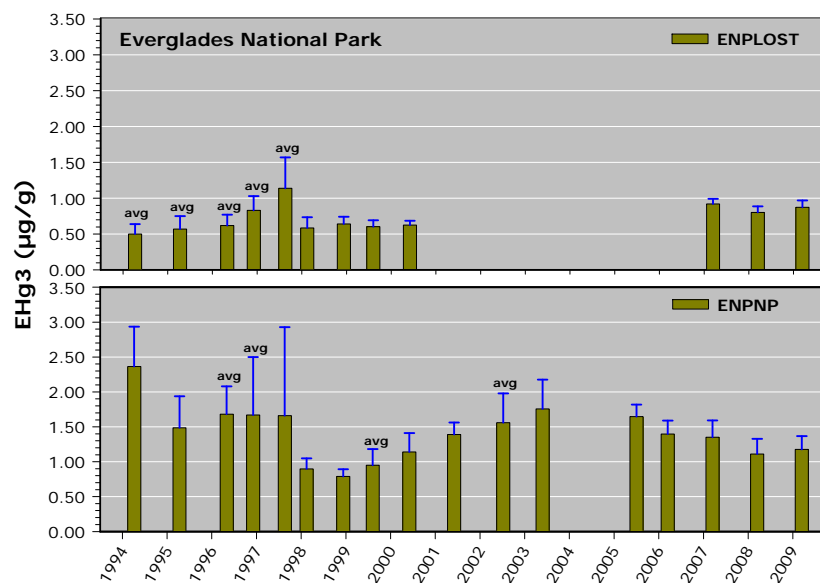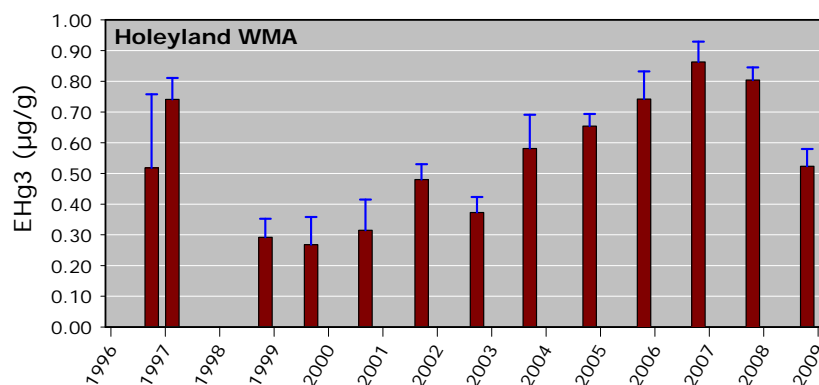
Figure 3B-10. Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval in LMB at long-term monitoring sites located within the Holey Land Wildlife Management Area.
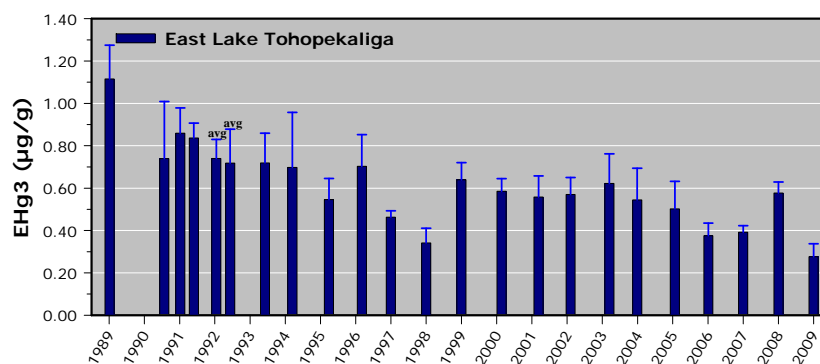
Figure 3B-11. Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval in LMB at long-term monitoring sites in East Lake Tohopekaglia.
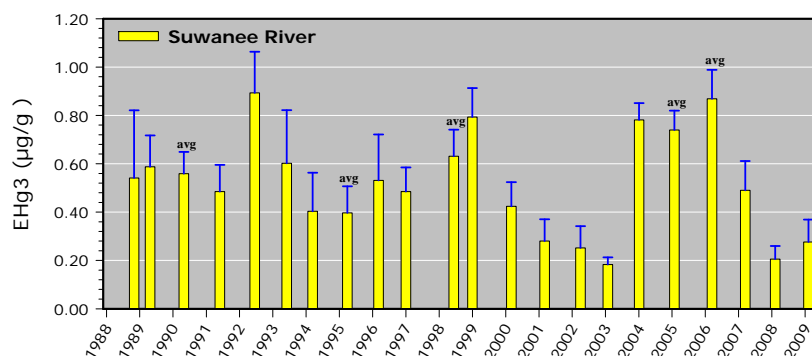

Figure 3B-12. Age-standardized mercury concentration (EHg3) and the 95 percent confidence interval in LMB from the lower Suwannee River long-term monitoring site at Fowler's Bluff. The average THg concentration (avg) is reported where calculation of the EHg3 were not appropriate.

Trends in the Kissimmee Basin

The bioaccumulation of mercury ranks as one of the major water quality issues in the Kissimmee Basin. Mercury bioaccumulation poses a health risk for humans and wildlife due to consumption of contaminated fish. Twenty water bodies in the Kissimmee Basin are under some level of public health advisory on the Limited Consumption Advisory list (Florida Department of Health, 2007). Also, the FDEP has verified 11 lakes in the Upper Kissimmee Basin as impaired for mercury in fish tissue.

Because mercury contamination is thought to result from atmospheric deposition originating from external sources, such as fossil fuel power plants and municipal and medical waste incinerators, solutions to this problem are being addressed by the FDEP and the USEPA. For this reason, the SFWMD is not currently monitoring Hg in the Kissimmee Basin. However, the District uses data on THg concentrations in fish tissue data collected by the Florida Fish and Wildlife Conservation Commission (FWC).

The SFWMD has examined THg data collected by the FWC in the Kissimmee Basin from 1987–2008. Fish were collected by electroshocking, and tissue data were collected in accordance with the FDEP SOP FS6000 (General Biological Tissue Sampling) and FS 6200 (Finfish Tissue Sampling). This method of subsampling involves sectioning half-inch strips of fish muscle tissue taken from a fillet of dorsolateral muscle on the posterior portion of the body of the fish. The tissue is rinsed with analyte-free water and stored in a culture tube at -20ºC until shipping or analysis. THg is measured using cold vapor atomic absorption spectroscopy according to USEPA Method 245.6.

Analysis of the FWC mercury data was problematic because the number of each species in a body of water caught ranged from one to 40 fish. Since the FDEP uses data from fish collected over the previous 7.5-year period for identifying impaired waters, it is not necessary to collect samples every year from every water body. However, a larger and more representative dataset would be needed for a definitive analysis of mercury levels in the Kissimmee Basin. It is also important to determine a baseline toxicity level in the Kissimmee Basin.

The species for which most data were obtained was largemouth bass, an abundant and popular sport and food fish. As such, the LMB serves as the sentinel species in this report. This species is also a logical focus for analysis of mercury contamination because of its relatively higher levels of mercury due to its size and high trophic position. This analysis only uses data for bass that are legally harvestable under regulations for Northeastern and Central Florida (larger than 14 inches), since this size class is being consumed by the public most regularly. The most extensive samples contained fish collected from Lake Tohopekaliga and East Lake Tohopekaliga. Therefore, the data for these lakes will be discussed in the greatest detail. However, data for all sampled lakes are presented in **Table 3B-3**.

For the available period of record, the range of mean annual THg levels in the LMB from East Lake Tohopekaliga was 0.52–1.34 micrograms per gram (µg/g) between 1989 and 2008. Overall, the data indicated a decline of 35.8 percent between the peak in 1990 and the most recent collection in 2008 (**Figure 3B-13**). In Lake Tohopekaliga, the range of mean annual THg for LMB was 0.38–0.77 µg/g, with a decrease of 50.6–75 percent in mean THg from 1989 to 2008 (**Figure 3B-14**). Where data are available for multiple years, every water body in the basin indicates declining mercury levels in LMB (**Table 3B-3**).

Still, mercury in fish remains high throughout the basin. When the average mercury levels in a species exceeds 0.2 µg/g, FDEP issues a Limited Consumption Advisory for that species in the specified body of water. At this level, LMB should be consumed no more than once a week, or once a month for children and women of childbearing age. In the most recent year of data, all water bodies in the Kissimmee Basin tested above this level. The Kissimmee Chain of Lakes that

have the highest mean THg levels (Alligator, Brick, Gentry, Hart, and Mary Jane) ranged in concentrations of 1.06–1.46 µg/g, falling under a higher level of advisement in which LMB should be eaten no more than once a month, and not at all for children and women of childbearing age.

A more robust dataset would be needed for thorough statistical analysis, including a more consistent sampling of other species. Despite these limitations, a decrease in Hg levels across the Kissimmee Basin is suggested by the 1987–2008 data. This decline is likely due to legislation and regulations enacted in the early 1990s which reduced mercury content of wastes and limited emissions from Florida municipal solid waste combustors and medical waste incinerators. Although this trend seems promising, as of 2008, Hg levels in LMB and other large-bodied piscivorous fish remain at or above cautionary levels throughout the Kissimmee Basin.

Table 3B-3. Overview of total mercury (mg/kg; wet weight tissue) averages in largemouth bass during various periods of record in the Kissimmee Basin and. Trends in mercury levels are described as a percent change from the maximum reported average.

Location	Reported POR	Sample Events	Maximum THg	Year	Most Recent THg	Year	Percent Change from Maximum
Upper Basin							
Alligator Lake	1990-2004	2	1.42	1990	1.28	2004	-9.9
Brick Lake	1989-2004	3	1.37	1989	1.09	2004	-20.4
Cypress Lake	2004	1	0.52	2004	0.52	2004	NA
East Lake Tohopekaglia	1989-2008	20	1.34	1989	0.86	2008	-35.8
Lake Gentry	2002-2004	2	1.27	2004	0.87	2005	-31.5
Lake Hart	1991-2005	3	1.46	2003	1.03	2005	-29.5
Lake Hatchineha	1990-2004	3	1.18	1990	0.59	2004	-50
Lake Kissimmee	1991-2005	2	0.62	1989	0.58	2003	-6.5
Lake Mary Jane	2003	1	1.06	2003	1.06	2003	NA
Lake Marian	2002	1	0.36	2002	0.36	2002	NA
Lake Russell	2002	1	0.74	2002	0.74	2002	NA
Lake Tohopekaglia	1989-2008	19	0.77	1989	0.38	2008	-50.6
Tiger Lake	2003	1	0.39	2003	0.39	2003	NA
Lower Basin							
Kissimmee River	2004	1	0.61	2004	0.61	2004	NA

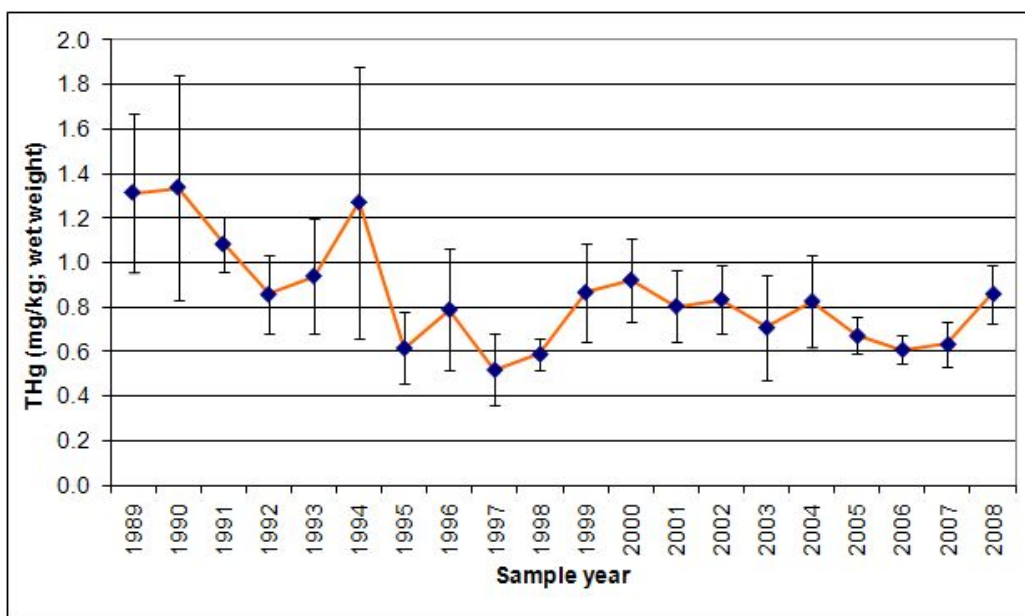**Figure 3B-13.** Average total mercury levels (mg/kg; wet weight tissue) ± one SD of largemouth bass in East Lake Tohopekaliga from 1989–2008. Individuals were of legally harvestable size (>14 inches).
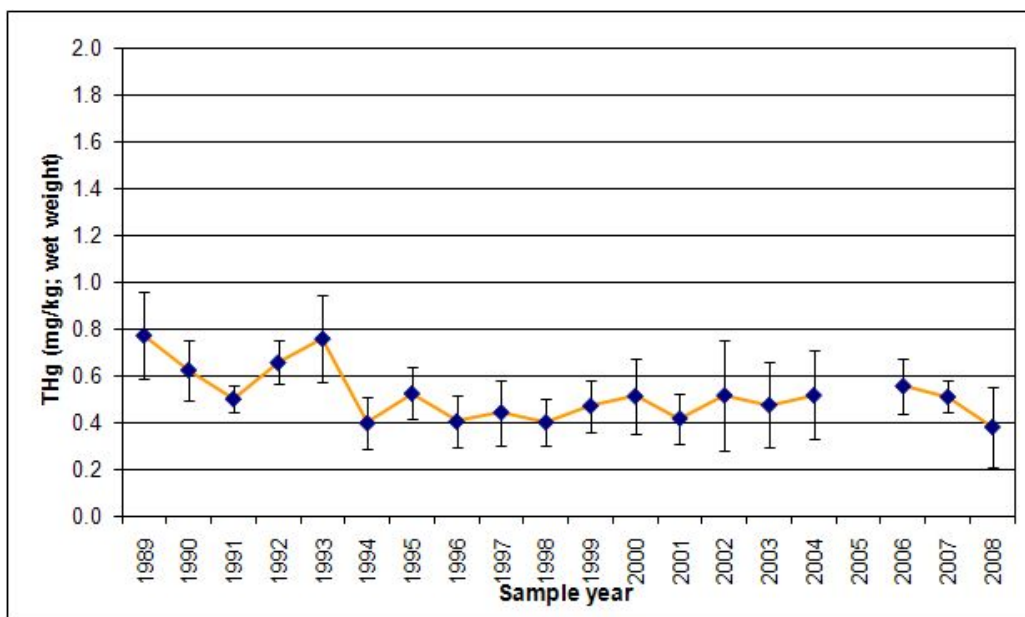

Figure 3B-14. Average total mercury levels (mg/kg wet weight tissue) ± one SD of largemouth bass in Lake Tohopekaliga from 1989–2008. Individuals were of legally harvestable size (>14 inches).

SULFUR LEVELS, SOURCES AND EFFECTS
ON THE EVERGLADES

Elevated levels of MeHg, a highly toxic and bioaccumulative form of mercury (Driscoll et al., 2007; Munthe et al., 2007), were first reported in biota from the ENP in 1974 (Ogden, 1974). In 1988, reports of mercury levels in LMB in the WCAs exceeding 1 mg/kg prompted more widespread sampling of both fish and wildlife (Ware et al., 1990).

In response to concerns over these elevated levels of MeHg, the U.S. Geological Survey (USGS) established the Aquatic Cycling of Mercury in the Everglades (ACME) Group. ACME is a component of the federal contribution to the state/federal effort to restore the Everglades by improving both the quantity and quality of water in the Everglades — a major goal of the Comprehensive Everglades Restoration Plan (CERP). The aim of ACME is to gain an understanding of the processes controlling the production of MeHg in the ecosystem and its bioaccumulation in fish and fish-eating wildlife.

To complement research and activities conducted by the ACME group, the Sulfur Action Plan was established in 2007. The Sulfur Action Plan is a multi-agency research initiative led by the SFWMD and partnering agencies. Investigations under the Sulfur Action Plan are used to determine the potential impacts of sulfur to plant toxicity, nutrient mobilization, mercury bioaccumulation and the overall fate and transport of sulfur in the EPA. The chapter sections *Regional Sulfur Mass Balance Study* and *Evaluation of Sulfate Effects in South Florida Wetlands* detail introductory results under the plan. Additional research results from the Sulfur Action Plan are anticipated to be reported in future SFERs.

From studies conducted in other ecosystems, it was known that sulfate-reducing bacteria were important agents for the production of MeHg, and that dissolved organic carbon was an important factor promoting MeHg production. Hence, biogeochemical studies of mercury, sulfur, and carbon and the interactions of these elements within the Everglades environment were an original part of the ACME plan. ACME field studies began in 1995, with USGS scientists W. Orem (sulfur), D. Krabbenhoft (mercury), and G. Aiken (carbon) conducting coordinated efforts with C. Gilmour (Smithsonian Institution) conducting microbiological studies of MeHg production.

One of the most surprising findings to come out of the early ACME studies was the discovery of high levels of sulfur in the South Florida ecosystem. Sampling at a site in Water Conservation Area 2A, ACME investigators were struck by the strong "rotten egg" odor of hydrogen sulfide. The presence of hydrogen sulfide is unusual for a freshwater wetland – it is more characteristic of marine or estuarine systems. It was also evidence that microbial sulfate reduction was taking place and could be driving production of MeHg from inorganic mercury. Sulfate-reducing bacteria are the predominant producers of MeHg in aquatic ecosystems (Compeau and Bartha, 1985; Ekstrom et al., 2003; Gilmour et al., 2004).

While freshwater wetlands typically have low sulfate concentrations (Wetzel, 1975); sulfate concentrations in Everglades surface waters are high due to major inputs of sulfate to the ecosystem from the discharge of high conductivity, high sulfate concentration Everglades Agricultural Area (EAA) canal water (Orem, 2004). Everglades surface water sulfate concentrations follow a north-to-south gradient from the EAA to the freshwater ENP, with sulfate levels farther north in these marshes often exceeding 100 times historical levels; that is, levels in parts of the ecosystem further south and away from canal discharges (Bates et al., 2002; Gilmour et al., 2007a; Weaver et al., 2007). In general, Lake Okeechobee has annual average sulfate concentrations less than half of those in EAA canals (Bates et al., 2002), and thus the EAA has the highest sulfate concentrations across the Greater (freshwater) Everglades.

Sulfide in soil porewater shows a north-to-south gradient similar to that for sulfate in surface water, with extremely high porewater concentrations (up to 12,000 μg/L) in the north and low concentrations (0.1 μg/L) in the south. The extent of Everglades sulfur contamination has been documented by the USGS, the USEPA, the FDEP, and the SFWMD (Orem et al., 1997; Stober et al., 2001; Bates et al., 2001, 2002; Scheidt and Kalla, 2007; Payne et al., 2009).

ACME scientists originally hypothesized that the high levels of sulfate in Everglades surface waters downstream of the EAA originated from saline groundwater known to lie deep under the ecosystem. However, geochemical analyses of surface water and groundwater, including isotope tracer studies, showed that the sulfate entering the ecosystem did not appear to originate from groundwater. Results of isotope studies were consistent with sulfur applied to EAA agricultural soils (both new agricultural additions and legacy sulfur in EAA peat soils) as being the principal source of the sulfate entering the ecosystem (Bates et al., 2002; Orem, 2004; Axelrad et al., 2007; Gilmour et al., 2007b; Gabriel et al., 2008).

Sulfur has several roles in EAA agriculture. It is a plant nutrient; it is used as a fungicide; and sulfur is also present in some fertilizers as a counter ion to the principal nutrient. Possibly the greatest use of sulfur in the EAA is as a soil amendment for pH adjustment (Boswell and Friesen, 1993). Elemental sulfur acidifies soil and, by reducing soil pH, increases the availability of micronutrients. When soil pH exceeds 6.6, recommendations are to apply 500 pounds per acre (lb/acre) for muck and sandy mucks, 300 lb/acre for mucky sands, and no sulfur for sands (Rice et al., 2006). Actual sulfur usage in the EAA is estimated to be 30–100 lb/ac every three years (Wright et al., 2008).

Sulfate sourced from the EAA is not efficiently removed by the Stormwater Treatment Areas (STAs) via uptake by plants and subsequent loss to STA soils; STA removal efficiency is about 10 percent for sulfate versus 70 percent for phosphorus (Pietro et al., 2009). This is because the mass of inflow of sulfate-sulfur to the STAs exceeds that of total phosphorus by a factor of over 1,000, while as a nutrient, sulfur is required by plants in only about the same amounts as phosphorus (Beaton, 1966; Tabatabai, 1984).

The disparity in sulfate versus phosphorus loading to the EPA via the STAs is apparent in that while about 30 percent of the area of surface waters in the marsh exceed the 10 μg/L total phosphorus water quality standard, about 60 percent exceed the 1 mg/L (1,000 μg/L) sulfate-sulfur CERP goal (Scheidt and Kalla, 2007).

Field surveys have shown that sulfate stimulation of MeHg production and sulfide inhibition of this process explain the observed distributions of MeHg in Greater Everglades soils (where it is largely produced) and in fish across the ecosystem (Gilmour et al., 1998; Benoit et al., 2003; Gilmour et al., 2007a). Field surveys also documented the important role of dissolved organic carbon in complexing inorganic mercury (keeping it solubilized in water) for transport to sites where mercury methylation occurs (Gilmour et al., 2007a).

As indicated by a number of studies ranging in scale from laboratory microcosms to whole watershed manipulation, the relationship between mercury methylation and mercury inputs generally appears to be linear. This concept of linearity has also been demonstrated in the Everglades region through various laboratory and field mesocosm experiments conducted by ACME (Gilmour et al., 2007a). Given the essential linearity of this relationship, when one examines the degree to which methylation rates vary in relation to inorganic mercury concentrations in surficial sediments, it becomes quite clear that other variables are controlling the variance of methylation rates across the landscape. For example, THg concentrations in surface soils vary by a factor of approximately three, while MeHg concentrations in soils vary across the Everglades region by a factor of over 100 (Benoit et al., 1999 ; Cleckner et al., 1999; Gilmour et al., 1998, 2000, 2003, and 2004; Krabbenhoft et al., 2000; Rumbold and Fink, 2006).

As a result, the correlation between inorganic mercury and MeHg concentrations in Everglades soils is weak. In contrast, other environmental variables, such as surface water sulfate and total phosphorus, which both have the potential to influence methylation rates, vary in concentration across the Everglades region by factors of 26 (total phosphorus) to nearly 10,000 (sulfate) (Scheidt and Kalla, 2007).

Documented experimental investigation demonstrates that variations in sulfate may strongly influence the variations of methylation rates observed across the Greater Everglades. Field investigations as well as laboratory microcosm experiments conducted by ACME demonstrate clear linkages between sulfate and mercury methylation (Gilmour et al., 2004; Gilmour et al., 2007a). Therefore, reductions in sulfate loading may result in declines in MeHg production in the Everglades (Gilmour et al., 2004; Gilmour et al., 2007a), as has been demonstrated for the former MeHg hotspot, station 3A-15 in central Water Conservation Area 3 (Axelrad et al., 2005).

In order to decrease MeHg levels in Everglades fish and reduce the risk of exposure to toxic MeHg to anglers and fish-eating wildlife (FDOH, 2008; Rumbold et al., 2008), both reductions in atmospheric deposition of mercury and decrease in sulfur loading to the Greater Everglades should be considered as management options. There is increasing evidence that mercury sourced to the Everglades from atmospheric deposition is now predominantly from global rather than local (within Florida) sources (Atkeson et al., 2005; Axelrad et al., 2007 and 2008; Pollman et al., 2007). This makes examination of options for reducing sulfur loading to the Everglades as a means of reducing Everglades MeHg levels increasingly important.

To determine if it is feasible to reduce Everglades sulfur loading adequately enough to decrease MeHg levels in resident fish to an acceptable level, the sources of sulfur to the ecosystem must first be quantified. Gabriel (2009) and Wright et al. (2008) have recently produced sulfur mass balance estimates for the Everglades. (See the *Research Progress* section of this chapter.) For the EAA, comprising about 700,000 acres with 430,000 acres under crop production (IFAS, 2007), these estimates include sulfur sources such as: EAA peat soil oxidation, agricultural sulfur application, Lake Okeechobee inflow to the EAA, and atmospheric deposition of sulfur. Sulfur losses include outflow of sulfur from EAA canals to the EPA and harvesting of EAA crops.

For the EAA, estimates of selected major total sulfur fluxes for a wet year (2004), an intermediate rainfall year (2003), and a dry year (2007) are shown in **Table 3B-4**.

Table 3B-4. Total sulfur (TS) fluxes, in thousands of metric tons per year
in the Everglades Agricultural Area (from Gabriel, 2009).

Rainfall Year	Wet	Intermediate	Dry
TS canal in (from Lake Okeechobee)	41	31	28
TS canal out (to the Everglades Protection Area)	107	102	25
TS from agricultural application	6	6	6
TS from Everglades Agricultural Area soil oxidation	31	31	31
TS from atmospheric deposition	3	4	4
TS removal by crop harvest	26	26	26

As has been hypothesized previously, during a dry year much of the sulfur applied to EAA soils or released from these soils by oxidation may remain in place in the absence of adequate rainfall to wash the sulfur into EAA canals, and thus EAA canals and Lake Okeechobee waters have equivalent sulfate concentrations (Bates et al., 2002).

For wet and intermediate rainfall years, total sulfur flux from canal waters flowing out of the EAA into the EPA is two-to-three times greater than the total sulfur flux from Lake Okeechobee into the EAA, showing that the EAA is a major source of total sulfur to the EPA. Sources of sulfur to EAA canals include agricultural application, EAA soil oxidation, and wet and dry atmospheric sulfur deposition (though atmospheric deposition is a minor input). The major proximate sources of sulfur to the EAA must be determined to assess the feasibility of reduction in sulfur loading to the Everglades to reduce MeHg levels.

Regarding sources of sulfur to Lake Okeechobee, McCormick and James (2008) estimated that 98 percent of annual average sulfur load to Lake Okeechobee is from surface water inputs. Of this, 36 percent of the annual average sulfur load to the lake was estimated to be from the EAA during the period of record from 1974–2006. However, it should be noted that EAA contributions dropped sharply after backpumping was restricted in 1983 (McCormick and James, 2008). Estimates of annual average sulfur inputs to the lake from other sources are 28 percent from the Indian Prairie/Lake Istokpoga basin, 18 percent from the Kissimmee River, and 18 percent from other basins. Zielinski et al. (2006) note that improved beef cattle pastures account for approximately 36 percent of the Lake Okeechobee Watershed, and unimproved pastures and rangeland account for 15 percent of the watershed. Three estimates of total annual input of sulfur from Lake Okeechobee to the EAA are 39,000, 31,000 and 27,000 metric tons from Gabriel (2009), McCormick and James (2008), and Schueneman (2001) respectively.

For determining EAA sulfur mass balance, Gabriel (2009) estimated that agricultural applications of sulfur in the EAA averaged 20 lb of sulfur per acre per year, based on a weighted mean of sulfur applied to various crop types. Wright et al. (2008) used 33 lb of sulfur per acre per year in their calculations based on the estimates of Schueneman (2001); that estimate was derived from interviewing several EAA growers and sellers of fertilizer in the EAA region.

Releases of sulfur from oxidation of EAA soils occurs at an accelerated rate because much of the EAA is pumped dry to allow crop production (IFAS, 2007). The resultant oxic conditions

result in the relatively rapid loss of organic matter in EAA soils as compared with the rate of loss in flooded EPA soils. Gabriel (2009) reported that the EAA soil oxidation rate resulted in soil losses ranging from 0.5 to 1.5 inch/year while Wright et al. (2008) reported about 0.5 inch/year, the number used by Schueneman (2001) for sulfur mass balance estimates. The oxidation of organic sulfur in EAA soils allows sulfate to be washed into EAA canals during rain events (Bates et al., 2002).

Determining the sources of sulfur in EAA soils bears upon options for reducing sulfur loading to the Everglades. Gabriel (2009) notes that total sulfur concentrations range from 0.1–5 percent in soils across the EAA. Organic sulfur, the largest fraction of the total sulfur in peat soils from the freshwater Everglades, accounts for 50–85 percent of the total sulfur at most locations (Altschuler et al., 1983; Bates et al., 1998). Organic sulfur forms through the reaction of sulfide with soil organic matter, and thus it is plausible that some or even most of the organic sulfur in EAA peat soils results from the reaction of agricultural applications of sulfur with soil organic matter (Bates et al., 2002).

Presently available EAA sulfur mass balance estimates show a range of oxidation rates. Gabriel (2009) estimates that sulfur sourced from EAA soil oxidation exceeds sulfur from agricultural application to EAA soils by a factor of five; Wright et al. (2008) estimates that ratio at 11, and Schueneman (2001) estimates the ratio at 15. Estimates vary greatly because of uncertainties in the actual amounts of all forms of sulfur added to EAA soils, and average sulfur contents and oxidation rates of EAA soils.

While sulfur contamination has increased MeHg levels in Greater Everglades fish (Gilmour et al., 2007a, Gabriel, 2009), there are at least two other significant environmental concerns regarding sulfur. First, sulfur as sulfate or sulfide effects the biogeochemical cycling of numerous elements; sulfate, via a process termed internal eutrophication, may cause the release of phosphorus and nitrogen from wetland soils (Lamers et al., 1998; Smolders et al., 2006). There is preliminary evidence of sulfate-induced internal eutrophication in the Everglades (Gilmour et al., 2007b), and further research is being conducted on this topic.

Second, sulfide is toxic to aquatic plants (Mendelssohn and McKee, 1988; Koch and Mendelssohn, 1989) and aquatic animals (National Research Council, 1979). Li et al. (2009) hypothesized that sulfide toxicity could in part be responsible for the replacement of native sawgrass (*Cladium jamaicense*) by cattail (*Typha* spp.) in the Greater Everglades. Recent data (W. Orem, USGS, personal communication, 2009) from northwest WCA-2A indicate that surface water levels of undissociated hydrogen sulfide are many times higher than the USEPA's recommended water quality criterion for ambient waters (maximum 2 μg/L undissociated hydrogen sulfide for protection of fish and other aquatic life). This is consistent with hydrogen sulfide data from surface waters from WCA-2A as reported by Orem et al. (1997).

Of the three detrimental environmental effects of sulfur (increase in MeHg production, internal eutrophication, and sulfide toxicity) it is likely that increased MeHg production occurs (at lower sulfate concentrations) before the other two effects. There is thus a need for refined Everglades sulfur mass balance estimates in order to determine if it is feasible to reduce sulfur loading to the point of enhancing efforts to lower MeHg to acceptable levels for public health and fish-eating wildlife.

INFORMATION NEEDS AND RECOMMENDATIONS

Information needs and recommendations regarding Everglades sulfur source determination and management include:

- Implement high resolution spatial sampling frameworks over various time periods to capture particular meteorological conditions (i.e., dry, wet, and intermediate seasons) with more frequent measurement of sulfur flux past District structures in the Everglades to better determine sulfur inputs to various areas of the ecosystem (Gabriel, 2009).

- Better estimate the quantity of agricultural applications of sulfur to soils in the EAA including applications previously not measured [e.g., sulfur-fungicide use; addition of gypsum ($CaSO_4$) for EAA soil erosion control].

- Accurately determine the rate of oxidation of EAA soil organic-sulfur, for oxic (dry) and anoxic (submerged soil) conditions.

- Quantify the reduction in rate of sulfur loss from EAA soils in the absence of agricultural sulfur application; determine the time for sulfur release from EAA soils to reach minimum value after cessation of agricultural sulfur applications.

- Estimate groundwater sulfur inputs to the EAA.

- Quantify the sources to and the sulfur mass balance for Lake Okeechobee.

- Review options for restoring the Everglades hydropattern while minimizing sulfur effects. The delivery of sulfate-contaminated water through the Everglades canal system to protected areas such as the ENP and the Arthur R. Marshall Loxahatchee National Wildlife Refuge – areas that previously did not have elevated levels of sulfur – may cause environmental harm; in contrast to moving water though the canal system, moving water as sheetflow over expansive marsh areas may allow for sequestration of reduced sulfur in soils and, thus, reduce the sulfate loads delivered to these protected areas (Orem, 2007).

- Review options for restoring Everglades region hydropatterns while minimizing sulfur effects. Current management practices have altered the natural drying and rewetting cycles of the system: soil drying results in the oxidation of reduced sulfur to sulfate; upon rewetting, a pulse of sulfate and MeHg production occurs (Gilmour et al., 2004; Orem, 2007).

- Review the potential effects of Aquifer Storage and Recovery on Everglades sulfur loading (Krabbenhoft et al., 2007).

- Estimate the cost and effectiveness of sulfur Best Management Practices for the EAA and Lake Okeechobee Watershed.

- Investigations aimed at improving sulfate removal by existing STAs should be initiated. Residence time of water in STAs is one key factor limiting removal of sulfate. Pilot studies of re-engineering STAs with iron-supplemented permeable reactive barriers (or other approaches) should be started. These mitigation strategies would complement strategies (BMPs, and prevention of soil oxidation) aimed at reducing sulfate from the EAA and Lake Okeechobee.

RESEARCH PROGRESS

The following research needs were identified in peer-review comments from previous Everglades Consolidated Reports (ECRs) and South Florida Environmental Reports (SFERs). An update on the progress made with respect to each of the research needs is presented below.

1. Quantify the no-effect level for Greater Everglades fish-eating bird dietary exposure to MeHg to support development of a water quality criterion (2000 ECR).

Following the FDEP's initial support for research on MeHg effects on white ibis (*Eudocimus albus*) (Frederick et al., 2005, 2007; Axelrad et al., 2008, 2009), the U.S. Fish and Wildlife Service and the U.S. Army Corps of Engineers (USACE) provided continuing funding. The final report to the USACE was submitted in December 2008 (Jayasena and Frederick, submitted).

In the study, experimental groups of 40 white ibises (even sex ratios) were exposed to 0.05, 0.1, and 0.3 mg MeHg/kg wet weight in diet from 90 days of age through three breeding seasons. No effects were found of MeHg on mass, size, survival, appetite, juvenile hormone levels, or the ability to learn to feed in novel situations.

However, all of the mercury-dosed groups had significantly lower reproductive success than the control group in all years, with up to 30 percent reduction in reproductive success. The main loss of reproduction was due to nests not producing eggs, and this stemmed directly from a high rate of male-male pairings (up to 55 percent of males), an effect which was dose-related in two of the three years.

The male-male pairings showed nearly all of the characteristics of male-female pairings, including phenology, courtship, copulation, nest construction, nest attendance, mate defense, and socially monogamous behavior. Male-male pairs were often of longer duration than male-female pairings, and dosed groups all had significantly more time (pair-days) spent in male-male pairings than did the control group.

In all years, the majority of the reproductive deficits in dosed groups were attributable to male-male pairing (2006: 75–85 percent, 2007: 82–100 percent, 2008: 50–100 percent). Male-male pairings were not a result of location effects, sex ratio, or constrained mating opportunities. Further, male-male pair bonds in all groups were formed relatively early in the breeding season at a time when there were unpaired females available in breeding condition.

Unpaired females often approached and attempted to court homosexual males but were rebuffed. Some homosexual males later formed heterosexual pair bonds in the same or subsequent seasons, and had fertile eggs in all of those situations, demonstrating that they were competent mates. Male-male pairings declined over the three breeding seasons, suggesting that birds were switching mates because of poor reproductive success.

Expression of sex steroids (estradiol and testosterone) were also affected by MeHg exposure, showing a dose-dependent response. The pattern of altered expression was exaggerated within any group among homosexual males, suggesting that MeHg-induced changes in hormone expression affected sexual behavior and pairing preference and, through that mechanism, reproduction was affected. While this experimental evidence strongly links hormones, mercury exposure, and behavior, the physiological mechanisms involved are unknown.

This study suggests that MeHg can function as an endocrine disruptor, resulting in altered sexual behavior and reduced reproductive success. The reduction in reproduction was not trivial – if the normal sex ratio in the wild is 1:1 the reduction in success could be up to 55 percent (the proportion of males pairing with males in this study). In many studies, effects seen in the lab are

exaggerated in the field because of additional stressors in the wild, and it is unclear whether effects documented in the aviary would be elevated in the Everglades.

At minimum, the implications of this study are that MeHg exposure at ambient levels in the Greater Everglades in the 1990s could have been enough to affect breeding behavior to the extent that measurable demographic change may have been realized. As mercury exposure declined in the late 1990s, the numbers of breeding pairs of wading birds increased by 3–5X. While some of this increase was clearly due to better hydrological conditions, hydropattern does not explain all of the increase, and mercury is an explanatory variable in nearly all models of population response during this period. While these results are merely correlational, the experimental research demonstrates an effect and a mechanism by which mercury affected populations.

In addition, it is worth noting that the lowest effects level (0.05 mg/L in diet) from this study is still commonly encountered by birds in the Greater Everglades today. Methylmercury appears to have a potentially powerful effect on reproduction in birds, and the effects research indicates it could strongly interact with other variables (e.g., hydrological restoration) to produce both masking and additive effects.

2. Quantify "global versus local" atmospheric mercury sources to South Florida to better define options for reducing mercury levels in Everglades biota (2002 ECR).

See the *Statewide Mercury Total Maximum Daily Load Program* section of this chapter.

3. Revise the Everglades Mercury Cycling Model (E-MCM) to include relationships between sulfur concentrations and mercury dynamics (2001 ECR).

The SFWMD has supported efforts to capture the biogeochemical relationships between the mercury and sulfur cycles in the Everglades Mercury Cycling Model (E-MCM), a mechanistic simulation model that runs on Windows™-based computers (Tetra Tech 1999a, b; 2002). From 2007–2008, E-MCM was used to simulate the MeHg response at site WCA3A15 to decreases in sulfate input over the last 10 years (1995–2005) (Gilmour et al., 2008). Model outputs supported the hypothesis that sulfate declines are driving at least part of the observed decline in MeHg at this site. These E-MCM simulations did not examine the role of sulfide concentrations, which are low at WCA3A15, on mercury cycling. A study is currently under way (funded by the Electrical Power Research Institute) to improve the treatment of several processes in the lake version of MCM (D-MCM), including the representation of sulfide-mercury interactions, photoreduction of inorganic Hg(II), photodegradation of MeHg, solid-phase partitioning of mercury, and uptake of MeHg by benthic organisms. The results of this study are directly transferable to the E-MCM. An overall objective is to develop a single set of equations for mercury cycling that can function reasonably across a wide range of conditions that includes the Greater Everglades, lakes, rivers, estuaries and marine environments.

4. Research biogeochemical controls on mercury methylation (2001 ECR).

Significant progress has been made in our understanding of biogeochemical controls on mercury methylation through research conducted by the USGS and the Smithsonian Environmental Research Center (SERC), through support by the USGS, the FDEP and the SFWMD. Findings are noted in Axelrad, et al. (2008). The USGS plans one more year of mercury biogeochemical research, as detailed in Axelrad, et al. (2008, 2009). Additionally, the FDEP has contracted with SERC for compilation and synthesis of ACME data.

5. Determine sulfur sources to and effects on the Everglades (2006 SFER).

See the *Regional Sulfur Mass Balance Study*, and *Evaluation of Sulfate Effects in South Florida Wetlands* sections of this chapter.

STATEWIDE MERCURY TOTAL MAXIMUM DAILY LOAD PROGRAM

By 2012, the FDEP is required to develop a mercury Total Maximum Daily Load (TMDL) for mercury-impaired waters of the state. In 2008, the FDEP initiated a multi-year statewide mercury TMDL study for fresh water that includes both atmospheric and aquatic field monitoring and modeling components. The mercury TMDL study consists of gathering and assessing a complex suite of data involving mercury atmospheric emissions and deposition (both wet and dry), and aquatic cycling data. It also involves conducting atmospheric and aquatic modeling to quantify the needed mercury reductions to address mercury-related impairment in state surface waters. Aquatic and atmospheric monitoring for the study began in late 2008.

The FDEP has developed a collaborative research team to undertake the freshwater mercury TMDL study. At this time, the collaborators are the FDEP, the University of Michigan Air Quality Laboratory (UMAQL, as the prime contractor to FDEP for the project), Atmospheric Research & Analysis (as a subcontractor to the FDEP contract with UMAQL), Aqua Lux Lucis, Inc. (as a subcontractor to the FDEP contract with UMAQL), the USEPA Office of Research and Development National Exposure Research Laboratory (USEPA ORD-NERL), USEPA Science and Ecosystem Support Division, the Florida Fish and Wildlife Conservation Commission (through contract with the FDEP), the Institute for Atmospheric Pollution of the National Research Council of Italy (as a subcontractor to the FDEP contract with UMAQL), Southern Company Services, Inc., Everglades National Park (the entity), Orlando County Environmental Protection Division, the University of Central Florida, the City of Jacksonville, Hillsborough County, and Broward County.

Elements of the Florida mercury TMDL study include:

- Comprehensive, highly temporally resolved measurements of wet and dry mercury deposition at four locations, along with a suite of tracers that may be used to associate deposition with sources. These sampling areas are referred to as supersites. The four supersite monitoring locations are Pensacola, Tampa, Jacksonville, and Davie. Additional wet deposition-only satellite sites are located, one each, in Orange County and the ENP research station.

- Identification of all significant sources of mercury within Florida (emissions inventory).

- Monitoring of 128 each of lakes and streams throughout Florida for mercury content in fish tissue and for a suite of water chemistry parameters for use in aquatic cycling modeling.

- Development of an empirical probabilistically based aquatic cycling model to link mercury deposition with bio-magnification in fish as a function of waterbody geochemistry.

- Conducting atmospheric modeling (both dispersion and receptor models) for the purpose of quantifying Florida mercury sources versus those sources outside Florida that must be quantified to satisfy the mercury TMDL.

- Conducting an assessment of the distribution and magnitude of mercury content in fish within the Everglades and how the distribution will change with changes in atmospheric emissions of mercury.

MERCURY IN COASTAL WATERS

Excessive concentrations of mercury have been found in fish for all of Florida's coastal waters, affecting numerous species of commercial or sport-fishing interest. Human health advisories regarding consumption of marine fish have been issued for about 60 species and there

are no-consumption advisories for several species for all of Florida's coastal waters. Floridians' exposure to MeHg is predominantly via consuming marine fish. The FDEP is seeking funding to determine the sources of mercury to the Gulf of Mexico and the most important sites of mercury methylation in the Gulf, through discussions with the USEPA together with representatives of the other four Gulf states, and with the Gulf of Mexico Alliance.

REGIONAL SULFUR MASS BALANCE STUDY

The objectives of the Regional Sulfur Mass Balance Study are to (1) quantify the source/sink and mass exchange characteristics of total sulfur (TS) and chloride (Cl⁻) between four major land-use areas of South Florida: Lake Okeechobee, EAA, Water Conservation Areas 1 and 2; (2) compare TS import/export flux magnitudes between surface (canal) flow, biogenic emissions, agricultural applications, agricultural harvesting (sugarcane), and atmospheric deposition; and (3) reevaluate each sulfur source. The mass transfer analyses include chloride (Cl⁻) due to its conservative transport properties. The Cl⁻ mass balance data will be used to investigate the percentage of TS lost or gained from physical and cumulative biogeochemical processes. Evaluating these objectives will provide source/sink characteristics of TS of each land-use area with respect to varying precipitation conditions and put into perspective the largest TS mass transfer mechanism for each land-use area.

Objectives 1 and 2 are executed by collecting information on surface water chemistry, atmospheric deposition, and surface flow from the District's DBHYDRO database and the USEPA's CASTnet. Information on agricultural sulfur applications, sugarcane harvest, and soil subsidence rates are obtained through literature review. On average, monthly to bi-monthly TS, Cl⁻, and SO_4^{2-} data are used for mass transfer calculations. Linear interpolation is used to identify sulfate (SO_4^{2-}), Cl⁻, and TS values for missing days. Canal water TS data in concert with sediment TS concentration is used to estimate TS carried by water column particulates in canals. Total sulfur mass transfer for each land-use area is calculated on an annual basis.

Thus far, three separate years have been investigated: a high precipitation year [2004 (556 cm)], a drought year [2007 (393 cm)] and an intermediate scenario [2003 (472 cm)]. The listed rainfall amounts are the total rainfall for all land-use areas combined. **Figure 3B-15** shows the stations used in the mass balance calculations. The stations listed account for 90 to 95 percent of the total surface (canal) flow for each land use area.

Figure 3B-16 shows TS and Cl⁻ loading results for each land-use area. As shown, the source/sink characteristics for TS and Cl⁻ varied considerably for each land-use area. For 2004 and 2003, WCA-1 and WCA-2 were significant TS sinks, Lake Okeechobee was a slight source, and the EAA was a major TS source. Chloride also shows similar source/sink characteristics for each land-use area; however, Cl⁻ loads are much greater than TS. In 2003, WCA-1 reversed and became a TS and Cl⁻ source. For 2007, loadings contrast significantly. Loadings to and from each land-use area were much lower than 2003 and 2004 and the difference between inflow and outflow loading is much smaller. In addition, in 2007 the source/sink signatures of the EAA and Lake Okeechobee reversed with respect to 2003 and 2004. **Figure 3B-16** also shows TS and Cl⁻ atmospheric deposition for each area. As shown, wet deposition is in some cases orders of magnitude larger than dry deposition for both TS and Cl⁻.
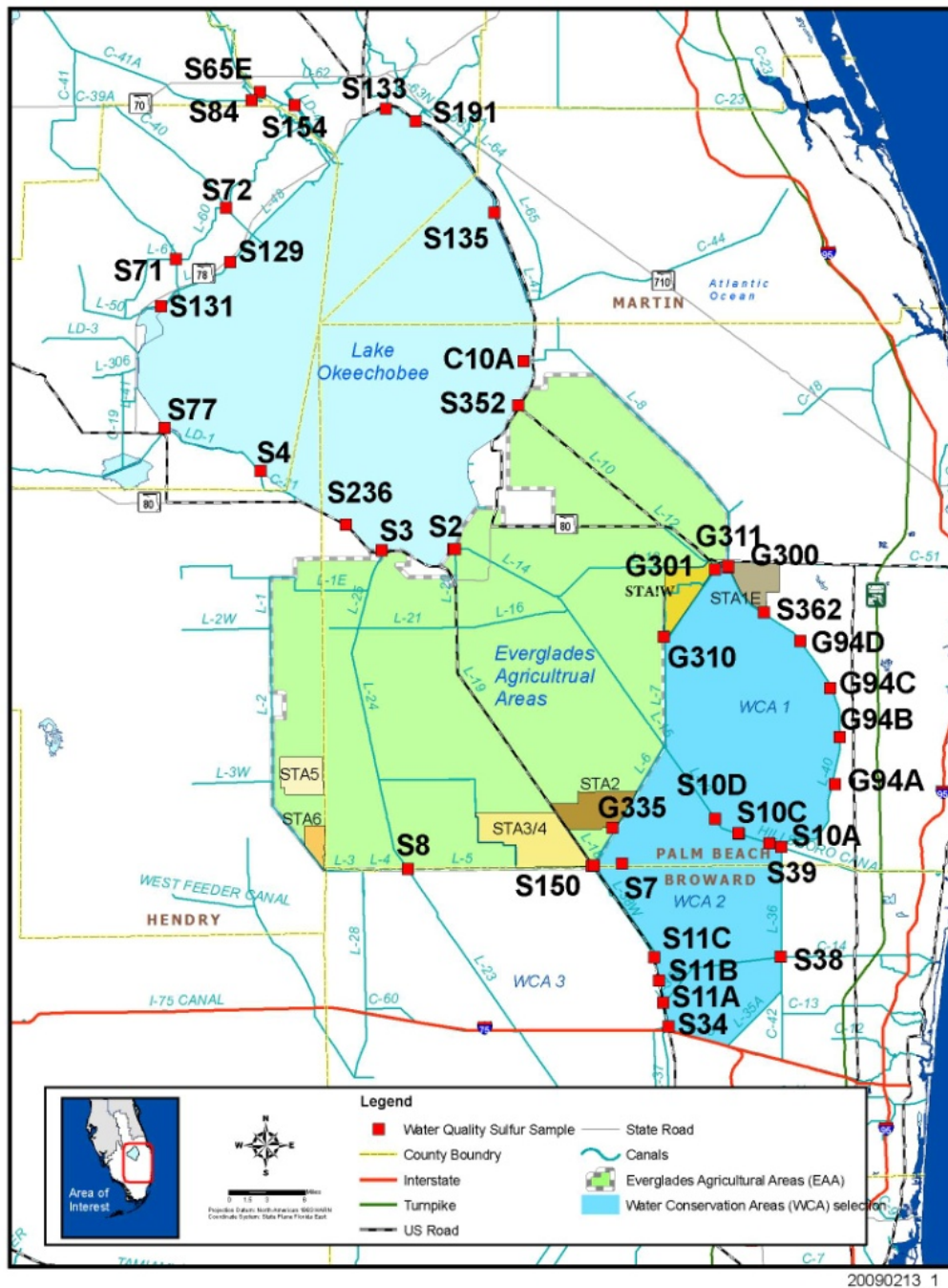
Figure 3B-15. Sulfate, chloride, total suspended solids, and flow measurement locations used in the mass transfer calculations.
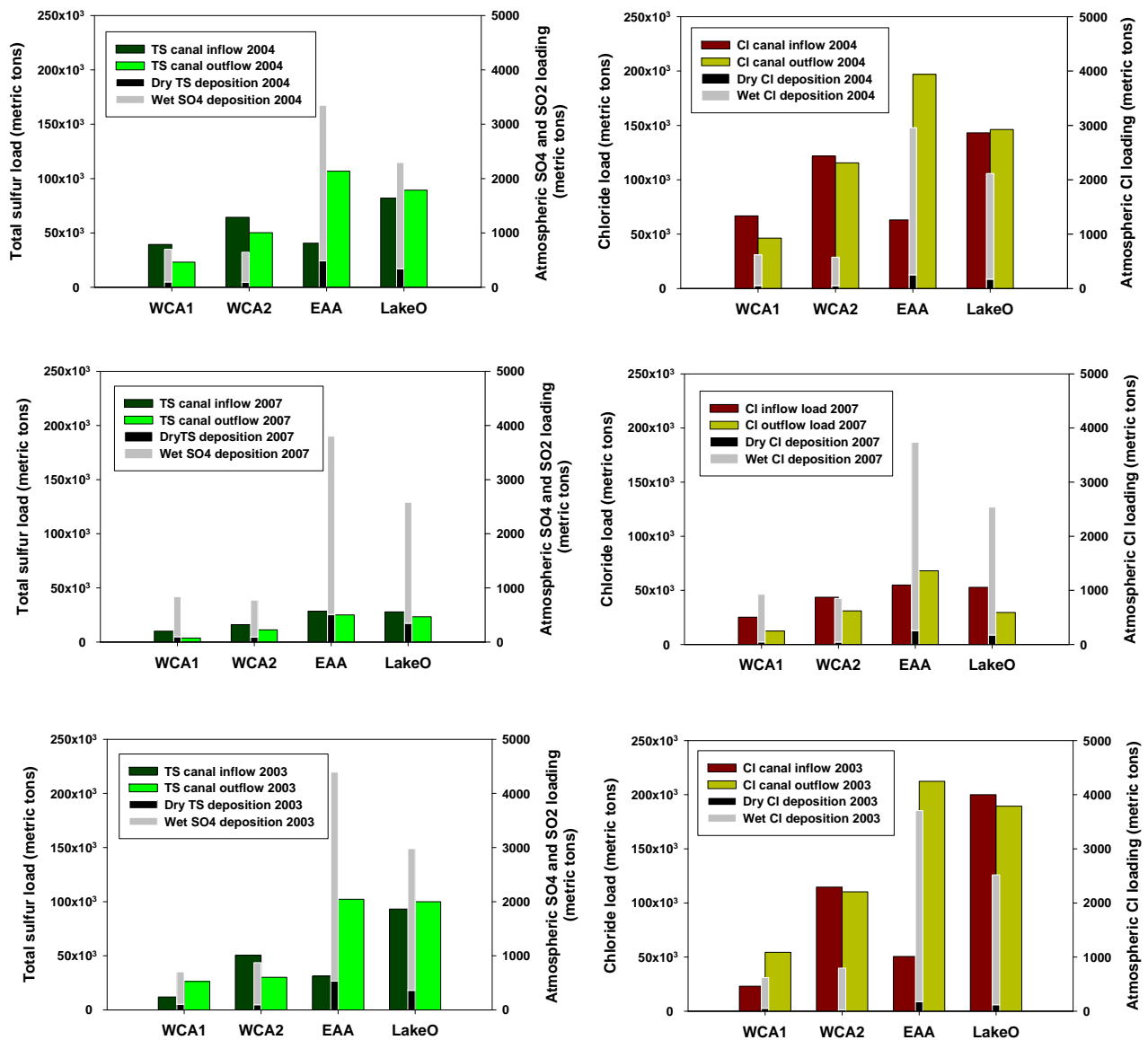
Figure 3B-16. Total sulfur and chloride loadings for each land-use area across three categories of rainfall: in dry year (2004), wet year (2007), and intermediate year (2003).

Figure 3B-17 shows loadings from each area expressed as a percentage of total load exchange. If a loading value lies above the 100 percent mark then the area is a TS source; if below 100 percent the area is a TS sink. Overall, the largest variation in source/sink characteristics is for WCA-1 and the EAA. Lake Okeechobee and WCA-2 show the least amount of variation from year to year. Not surprising, all loadings track water volume exchange. The difference between Cl⁻ and TS loading will be an area of further investigation.
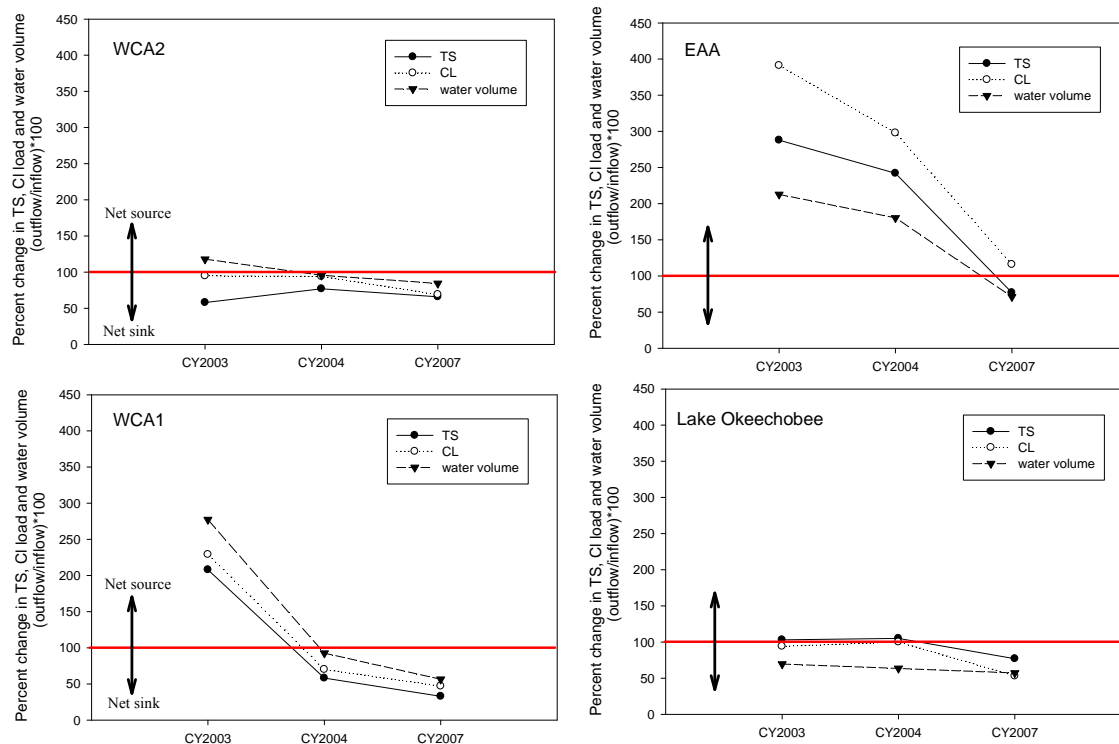

Figure 3B-17. Total sulfur and chloride loadings from each land-use area expressed as a percentage of the total inflow/outflow load.

The second objective of this study also entails performing a literature review on biogenic sulfur gas emissions, sulfur release from soil oxidation, sugarcane harvest, and agricultural sulfur applications, and comparing these values to TS magnitudes transported by canals. For biogenic sulfur gas emissions, the literature demonstrates hydrogen sulfide (H_2S), di-methyl sulfide (C_2H_6S), carbonyl sulfide (COS), and di-methyl di-sulfide ($C_2H_6S_2$) are the predominant reduced sulfur gases released from fresh and saltwater marshes. Ranges in flux are < 0.02 microgram per square meter per hour ($\mu g\ m^{-2}\ h^{-1}$) for individual species and up to 30 $\mu g\ m^{-2}\ h^{-1}$, cumulatively, for all species (Cooper et al., 1987; Castro and Dierberg, 1987; Giblin and Wieder, 1992; Hines et al., 1993; Delaune et al., 2002). For comparison to all other TS transport mechanisms, a value of 7.3 $\mu g\ m^{-2}\ h^{-1}$ (adapted from Giblin and Wieder, 1992) was used to represent total biogenic sulfur gas emissions for WCAs 1 and 2.

For TS transported out of the EAA from soil oxidation, the literature reports soil oxidation ranges between 0.5 to 1.5 inches per year (Schueneman, 2001; Wright et al., 2008; Snyder, 2005). This relatively wide range in soil oxidation rate exists primarily due to higher rates that occurred in the past. Currently, average soil oxidation rates are between 0.5 to 0.6 inches per year throughout the EAA (Schenueman, 2001; Snyder, 2005). The literature shows TS concentrations in EAA histosol soil range between 0.1 to 3 percent (Schueneman, 2001; Gilbert and Rice 2006; Chambers and Penderson, 2006; Wright et al., 2008; Guesch, 2007). Assuming a TS soil concentration of 0.37 percent (average value obtained from District data collections in 2004; see DBHYDRO project EAAD), an average soil bulk density of 250 kilograms per cubic meter (kg/m^3) and a soil oxidation rate of 0.5 inches per year (per communication with L. Fink), 109 kilograms per hectare per year ($kg\ ha^{-1}\ yr^{-1}$) was used to used to represent TS release from soil oxidation out of the EAA.

Regarding TS export out of the EAA from sugarcane harvest, approximately 17,000,000 tons of sugarcane is harvested from the EAA annually (Duke and Reisennauer, 1986; Baucum et al., 2006, Bates et al., 1998; Guesch, 2007). Assuming the TS content of sugarcane is 0.15 percent [TS concentrations in cattail/entire average 0.15 percent up to 0.30 percent (Duke and Reisennauer, 1986; Bates et al., 1998; Gesch et al., 2007)], this amounts to 25,500 metric tons of TS removed from the EAA annually. Agricultural-based sugarcane sulfur applications typically range between 18 and 33 lbs/ac, with University of Florida–Institute of Food and Agricultural Sciences (UF-IFAS) recommendations up to 500 lbs/ac (Schueneman, 2001; Gilbert and Rice, 2005; Wright et al., 2008; Rice et al., 2006). The range in sulfur applications exists due to yearly variations in sugarcane coverage across the EAA and soil pH. Sulfur applications for vegetable production are between 5 and 10 lbs/ac during a 90-day growing season (Schueneman, 2001; Wright et al., 2008). Therefore, using this information, an agricultural application value of 20 lbs/ac (22.45 kilograms per hectare per year) was used to represent total agricultural sulfur applications in the EAA.

The data collected from literature review was integrated over an annual basis and compared with TS through canal transport. **Table 3B-5** summarizes these results. For the moderate rainfall to high rainfall years (2003, 2004) the order of TS import/export magnitude for the EPA is as follows from largest to smallest: canal transport, sulfur release by soil oxidation, agricultural sugarcane harvest in the EAA, atmospheric deposition of TS, sulfur gas emission from WCAs 1 and 2. The EAA shows much greater importance for TS release by soil oxidation and sugarcane harvest during the dry year of 2007. Biogenic reduced sulfur emissions are almost negligible in comparison to all other transport mechanisms across all years. The largest variation in source sink characteristics across the studied years is for WCA-1 and the EAA (**Figure 3B-19**). TS source/sink characteristics remain relatively stable for Lake Okeechobee and WCA-2. Overall, these results show canal transport is the largest TS mass transfer mechanism for the South Florida ecosystem.

Table 3B-5. Summary of total sulfur (TS) mass transfer calculations for canals and literature review on all other import/export mechanisms; all data are in metric tons.

| Area	Canals TS (in)	Canals TS (out)	Atmospheric Dep (inches) Dry ($SO_4 + SO_2$)	Atmospheric Dep (inches) Wet (SO_4)	Biogenic S gas Emissions (out)	S Release by Soil Oxidation (out)	Sugarcane Harvest (out)	Agricultural S Applications (in)
2003								
WCA-1	11,911	26,287	102	600	*34*			
WCA-2	50,408	30,029	93	780	*35*			
EAA	31,057	102,214	529	3,864		*30,646*	*25,500*	*6,286*
Lake Okeechobee	93,101	99,824	359	2,622				
2004								
WCA-1	39,348	23,071	98	600	*34*			
WCA-2	64,319	50,269	91	555	*35*			
EAA	40,626	106,756	487	2,861		*30,646*	*25,500*	*6,286*
Lake Okeechobee	82,072	89,290	341	1,952				
2007								
WCA-1	9,935	3,548	97	740	*34*			
WCA-2	15,995	11,175	89	685	*35*			
EAA	28,494	24,961	508	3,295		*30,646*	*25,500*	*6,286*
Lake Okeechobee	27,756	23,300	345	2,236				
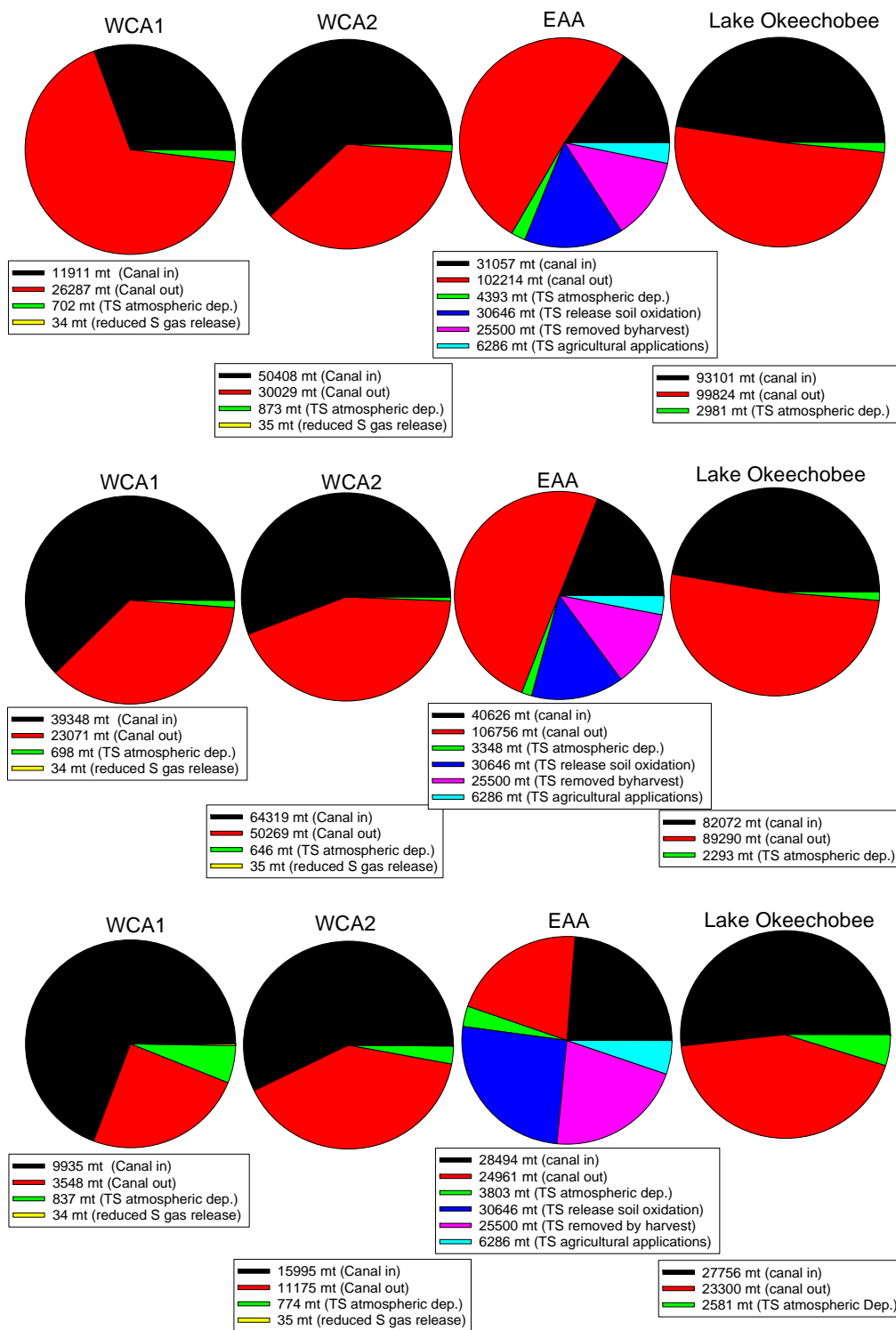
Figure 3B-19. Total sulfur mass transfer loadings for each land-use area during 2003 (top), 2004 (middle), and 2007 (bottom); units are metric tons.

The next steps of the study are to (1) further refine mass balance calculations, (2) further explore biogeochemical TS oxidation and reduction processes using chloride mass balance data, (3) include additional years in all analyses, (4) investigate the source for sulfur that contributed to the high SO_4^{2-} concentration at sampling locations, (5) perform a literature review on reduced sulfur gas emissions from Lake Okeechobee, and (6) further explore sulfur source delineation for the South Florida ecosystem.

Evaluation of Sulfate Effects in South Florida Wetlands

In order to assess if there are adverse ecological effects of sulfate in the Everglades regarding phosphorus release from sediments and sulfide toxicity to wetland plants, three projects are being funded by the SFWMD. Results for these projects are presented in Appendix 3B-2.

Project #1

Laboratory screening trials to determine the effects of elevated water column sulfate levels on microbial respiration and phosphorus release using soils collected from unimpacted and impacted (both phosphorus and sulfur) wetlands in South Florida. Objectives include:

1. Define the role of sulfate/sulfide on the release of sediment phosphorus (i.e., internal eutrophication) in South Florida wetlands.
2. Define the importance of sulfate/sulfide on organic matter mineralization in South Florida wetlands.
3. Better understand interactions between sulfur, calcium, and iron in wetland environments.
4. Assist in screening of treatments (e.g., appropriate chemical amendments and dosages) to be applied to subsequent mesocosm-scale experiments (see below).
5. Define accrual rates and diagenesis of sulfur, phosphorous, iron, and calcium in impacted and unimpacted sediments.

Project #2

Field monitoring to assess spatial and temporal variations in surface water and sediment porewater phosphorus and sulfur chemistry, and effects on wetland vegetation. The results obtained from the field monitoring and laboratory sediment phosphorus release studies will:

1. Provide necessary background information on the in situ concentrations of key elements and ions influenced by biogeochemical processes responsible for the sequestration/release of phosphorus.
2. Examine the spatial variability of elements and ions along sulfur and phosphorus gradients.
3. Characterize vertical concentration gradients within sediment and overlying water for calculating vertical diffusive fluxes.
4. Further the understanding of the role played by sulfate reduction in regulating phosphorus cycling.
5. Provide insight as to potential toxic effects of porewater sulfide on marsh flora.

Project #3

Mesocosm studies to evaluate plant toxicity and phosphorus cycling effects for a number of water, vegetation, and soil types. Objectives include:

1. Quantify the direct effects of sulfide and/or ammonium toxicity to native South Florida wetland flora.

2. Examine the effect of sediment history (e.g., high versus low phosphorus loadings) on internal phosphorus cycling and sulfur interactions.

3. Using flow-through, outdoor platforms, confirm results of laboratory incubations on effects on phosphorus cycling of varying calcium, sulfate, and phosphorus concentrations.

4. Characterize effects of inflow sulfate concentrations on the phosphorus removal effectiveness of the STAs.

Sulfate, Sulfide, Nutrient and Dissolved Organic Carbon Relationships to Methylmercury Production in the Everglades

Since 1995, the ACME project team – comprising USGS and SERC scientists – has studied mercury cycling in the Everglades.

Significant progress has been made in understanding biogeochemical controls on mercury methylation through ACME, supported by funding from the USGS, the FDEP, and the SFWMD. A summary of findings is presented in Axelrad et al. (2008).

The ACME study includes two main components. One is a detailed assessment, through time, of the biogeochemistry of core ACME sites across the full length of the Everglades ecosystem. These core sites include locations in each of the main components of the system, from the WCA-1 to the ENP.

The dataset for core ACME sites includes information on mercury and MeHg concentrations in surface water, soil interstitial waters (porewater), soils, and the food web. Food web components include invertebrates and small fish. Detailed biogeochemical data for the sites was also measured, including microbial activity and soils and water chemistry, with a focus on sulfur cycling and organic matter characterization.

The second component of the study is a series of field mesocosm experiments designed to test cause and effects hypotheses. Additions to mesocosms have included mercury, sulfate, dissolved organic carbon, and phosphate. Mesocosm experiments have been run in WCA-1, WCA-2, and WCA-3; the most detailed sulfate and dissolved organic carbon addition studies were carried out at site 3A15, WCA-3.

This project will compile data from all ACME researchers in one central database where it can be queried and studied as controls on sulfur inputs to the Everglades are debated. Metadata will be included. The dataset will be made accessible to the public (as well as submitted to the USGS for consideration for publication as an open file report). The project will also include a text report on the synthesized dataset.

As part of that report, a synthesis of the literature on MeHg production with a detailed focus on studies of the relationship between sulfate, sulfide, and MeHg will be produced. The literature summary will help to put the ACME datasets into a larger context, and provide information to decision makers.

SECOND ANNUAL WORKSHOP ON MERCURY AND SULFUR IN SOUTH FLORIDA WETLANDS

The Second Annual Workshop on Mercury and Sulfur in South Florida Wetlands was held at the South Florida Water Management District Headquarters on June 11–12, 2009. This workshop was organized by the SFWMD, the USGS, and the FDEP. The purpose of this workshop was to present data and conclusions from research conducted since the first annual workshop related to mercury and sulfur biogeochemistry and ecological effects in South Florida wetlands. This workshop was intended to support activities under the SFWMD's Sulfur Action Plan; the USGS' South Florida Ecosystem Program, and the FDEP's South Florida Mercury Science Program. Through these programs, the three agencies investigate the effects of elevated mercury and sulfur levels throughout the greater Everglades with research emphasis placed on mercury and sulfur interactions, internal eutrophication (sulfate-induced nutrient release from sediments), sulfide toxicity, agricultural applications of sulfur, and sulfur mass balance. A two-page USGS Fact Sheet or SFWMD technical publication is expected to be produced from this workshop. This document will be aimed at managers, legislators, and the public and will summarize conclusions from the meeting and suggest options for mitigating sulfur and mercury contamination in the Everglades.

ACKNOWLEDGMENTS

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